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(54) Title: CLEANING COMPOSITIONS COMPRISING A MYCODEXTRANASE

(57) Abstract

The present invention relates to cleaning compositions comprising a mycodextranase enzyme. Such compositions improve specific or broad stain removal, enhanced overall cleaning performance and sanitization of the treated surface.

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**CLEANING COMPOSITIONS COMPRISING A
MYCODEXTRANASE**

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TECHNICAL FIELD

10 The present invention relates to cleaning compositions including dishwashing, hard surface cleaning, toilet bowl cleaning and laundry compositions containing a mycodextranase enzyme.

15

BACKGROUND

15 The overall performance of cleaning compositions for use in washing or cleaning such as dishwashing, hard surface cleaning, toilet bowl cleaning and laundry, is judged by a number of factors, including the ability to remove soils and
20 the ability to prevent redeposition of the soils or the breakdown product of the soils on the articles being washed.

25 Food soils are often difficult to remove effectively from a soiled substrate. Highly colored soil derived from foods and/or beverages for example, tea or coffee, are particularly challenging to remove. Also body soils, especially menstrual fluids are difficult to remove completely and often build up on fabric, which leads to yellowing. The substrates, for example, can be dishes, hard
30 surfaces, toilet bowls or fabrics.

35 Enzymes have been added to cleaning compositions as a performance additive to improve cleaning performance. Enzymes can be included in the present cleaning compositions for a variety of purposes, including removal of

carbohydrate-based stains from surfaces such as textiles, for the prevention of refugee dye transfer in laundering, and for fabric restoration.

5 It has now been found that cleaning compositions comprising a mycodextranase enzyme improves specific or broad stain removal, boosts overall cleaning performance and provides sanitization for surfaces treated with the cleaning compositions of the present invention.

10

SUMMARY

The present invention relates to cleaning compositions comprising a mycodextranase enzyme. In further embodiments, the present invention further relates to cleaning 15 compositions comprising a mycodextranase enzyme in combination with selected detergent ingredients such as other enzymes, surfactants, bleaching agents and the like. Such compositions satisfy the need for a cleaning composition which provide improved specific or broad stain 20 removal, enhanced overall cleaning performance and sanitization.

DETAILED DESCRIPTION

An essential component of the cleaning compositions of 25 the present invention is a mycodextranase enzyme.

This mycodextranase enzyme is incorporated into cleaning compositions in accordance with the present invention at a level of from about 0.00001% to about 1%, preferably from 30 about 0.0001% to about 0.5%, as a pure enzyme by weight of composition.

Mycodextranase enzyme, which is 1,3- 1,4-alpha-D-Glucan 4-glucanohydrolase, is any enzyme which hydrolyzes 1,4- 35 alpha-D-glucosidic linkages in alpha-D-glucans containing

both 1,3- and 1,4- bonds. For example, mycodextranase enzyme hydrolyzes alpha-D-glucans into nigerose and 4-alpha-D-nigerosylglucose. Mycodextranase enzyme does not hydrolyze alpha-D-glucans containing only 1,3- or 1,4- bonds. Also mycodextranase enzyme have no hydrolyzation on the following glucans: alpha-1,4-(amlose), alpha-1,6-(dextran); beta-1,2-; beta-1,3-(laminarin); beta-1,4-(cellulose), beta-1,6-(pustulan). Mycodextranase enzyme is described in the following publications which are hereby incorporated by reference: E.T. Reese and M. Mandels, Canadian Journal of Microbiology, volume 10, pages 103-114 (1964); K.K. Tung, J. Biol. Chem., volume 246, number 22, pages 6722-6735 (1971).

15 Mycodextranase enzyme can be derived from fungal origin e.g. *Penicillium* species or can be expressed in any other suitable host organism via cloning techniques known in the art. This mycodextranase enzyme can be produced by the so called wild-type organism or by any host organism in which 20 the gene responsible for the production of the mycodextranase enzyme, has been cloned and expressed.

25 Nowadays, it is common practice to modify wild-type enzymes via protein / genetic engineering techniques in order to optimize their performance efficiency in the cleaning compositions of the invention. For example, the variants may be designed such that the compatibility of the enzyme to commonly encountered ingredients of such compositions is increased. Alternatively, the variant may 30 be designed such that the optimal pH, bleach stability, catalytic activity and the like, of the enzyme variant is tailored to suit the particular cleaning application.

35 In particular, attention should be focused on amino acids sensitive to oxidation in the case of bleach stability

and on surface charges for the surfactant compatibility. The isoelectric point of such enzymes may be modified by the substitution of some charged amino acids, e.g. an increase in isoelectric point may help to improve compatibility with 5 anionic surfactants. The stability of the enzymes may be further enhanced by the creation of e.g. additional salt bridges and enforcing calcium binding sites to increase chelant stability. Special care must be paid to the cellulases as most of the cellulases have separate binding 10 domains(CBD). Properties of such enzymes can be altered by modifications in these domains.

One preferred type of mycodextranase enzyme is a carbohydراse from the following EC category : EC 3.2.1.61, 15 which are commercially available by Sigma Chemicals. One DU unit liberates 1 micro mole of reducing sugar (measured as glucose) from nigeran per minute at pH 4.5 at 37°C.

Detergent components

20 The cleaning compositions of the invention may also contain additional detergent components. The precise nature of these additional components, and levels of incorporation thereof will depend on the physical form of the composition, and the nature of the cleaning operation for which it is to 25 be used.

The cleaning compositions according to the invention can be liquid, paste, gels, bars, tablets, powder or granular forms. Granular compositions can also be in "compact" form, 30 the liquid compositions can also be in a "concentrated" form.

The compositions of the invention may for example, be formulated as hand and machine dishwashing compositions, 35 hand and machine laundry detergent compositions including

laundry additive compositions and compositions suitable for use in the soaking and/or pretreatment of stained fabrics, rinse added fabric softener compositions, and compositions for use in general household hard surface cleaning 5 operations. Compositions containing such mycodextranase enzyme can also be formulated as sanitisation products, contact lenses cleaner and health and beauty care products such as oral/dental care and personal cleaning compositions.

10 Such compositions containing mycodextranase enzyme can provide fabric cleaning, stain removal, whiteness maintenance, softening, color appearance and dye transfer inhibition when formulated as laundry detergent compositions.

15

When formulated as compositions for use in manual dishwashing methods the compositions of the invention preferably contain a surfactant and preferably other detergent compounds selected from organic polymeric 20 compounds, suds enhancing agents, group II metal ions, solvents, hydrotropes and additional enzymes.

When formulated as compositions suitable for use in a laundry machine washing method, the compositions of the 25 invention preferably contain both a surfactant and a builder compound and additionally one or more detergent components preferably selected from organic polymeric compounds, bleaching agents, additional enzymes, suds suppressors, dispersants, lime-soap dispersants, soil suspension and 30 anti-redeposition agents and corrosion inhibitors. Laundry compositions can also contain softening agents, as additional detergent components.

35 The compositions of the invention can also be used as detergent additive products. Such additive products are

intended to supplement or boost the performance of conventional detergent compositions.

If the composition is a granule, the density of the 5 laundry detergent compositions herein ranges from 400 to 1200 g/litre, preferably 600 to 950 g/litre of composition measured at 20°C.

The "compact" form of the compositions herein is best 10 reflected by density and, in terms of composition, by the amount of inorganic filler salt. Inorganic filler salts are conventional ingredients of detergent compositions in powder form. In conventional detergent compositions, the filler salts are present in substantial amounts, typically 17-35% 15 by weight of the total composition.

In the compact compositions, the filler salt is present in amounts not exceeding 15% of the total composition, preferably not exceeding 10%, most preferably not exceeding 5% by weight of the composition.

20 The inorganic filler salts, such as meant in the present compositions are selected from the alkali and alkaline-earth-metal salts of sulfates and chlorides.

A preferred filler salt is sodium sulfate.

25 Liquid detergent compositions according to the present invention can also be in a "concentrated form", in such case, the liquid detergent compositions according to the present invention will contain a lower amount of water, compared to conventional liquid detergents.

30 Typically the water content of the concentrated liquid detergent is preferably less than 40%, more preferably less than 30%, most preferably less than 20% by weight of the detergent composition.

35 **Surfactant system**

The cleaning compositions according to the present invention comprise a surfactant system wherein the surfactant can be selected from nonionic and/or anionic and/or cationic and/or ampholytic and/or zwitterionic and/or 5 semi-polar surfactants.

The surfactant is typically present at a level of from 0.1% to 60% by weight. More preferred levels of incorporation are 1% to 35% by weight, most preferably from 10 1% to 30% by weight of the cleaning composition in accord with the invention.

The surfactant is preferably formulated to be compatible with the mycodextranase enzyme present in the composition. 15 In liquid or gel compositions the surfactant is most preferably formulated such that it promotes, or at least does not degrade, the stability of the mycodextranase enzyme, as well as other optional enzymes, in these compositions.

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Preferred surfactant systems to be used according to the present invention comprise one or more of the nonionic and/or anionic surfactants described herein.

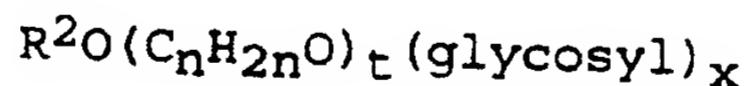
25 Polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are suitable for use as the nonionic surfactant of the surfactant systems of the present invention, with the polyethylene oxide condensates being preferred. These compounds include the condensation products 30 of alkyl phenols having an alkyl group containing from about 6 to about 14 carbon atoms, preferably from about 8 to about 14 carbon atoms, in either a straight-chain or branched-chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is present in an amount equal 35 to from about 2 to about 25 moles, more preferably from

about 3 to about 15 moles, of ethylene oxide per mole of alkyl phenol. Commercially available nonionic surfactants of this type include IgepalTM CO-630, marketed by the GAF Corporation; and TritonTM X-45, X-114, X-100 and X-102, all 5 marketed by the Rohm & Haas Company. These surfactants are commonly referred to as alkylphenol alkoxylates (e.g., alkyl phenol ethoxylates).

The condensation products of primary and secondary 10 aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use as the nonionic surfactant of the nonionic surfactant systems of the present invention. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and 15 generally contains from about 8 to about 22 carbon atoms. Preferred are the condensation products of alcohols having an alkyl group containing from about 8 to about 20 carbon atoms, more preferably from about 10 to about 18 carbon atoms, with from about 2 to about 10 moles of ethylene oxide 20 per mole of alcohol. About 2 to about 7 moles of ethylene oxide and most preferably from 2 to 5 moles of ethylene oxide per mole of alcohol are present in said condensation products. Examples of commercially available nonionic surfactants of this type include TergitolTM 15-S-9 (the 25 condensation product of C₁₁-C₁₅ linear alcohol with 9 moles ethylene oxide), TergitolTM 24-L-6 NMW (the condensation product of C₁₂-C₁₄ primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; NeodolTM 45-9 (the 30 condensation product of C₁₄-C₁₅ linear alcohol with 9 moles of ethylene oxide), NeodolTM 23-3 (the condensation product of C₁₂-C₁₃ linear alcohol with 3.0 moles of ethylene oxide), NeodolTM 45-7 (the condensation product of C₁₄-C₁₅ linear alcohol with 7 moles of ethylene oxide), NeodolTM 45-5 (the 35 condensation product of C₁₄-C₁₅ linear alcohol with 5 moles

of ethylene oxide) marketed by Shell Chemical Company, KyroTM EOB (the condensation product of C₁₃-C₁₅ alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company, and Genapol LA 030 or 050 (the condensation product of C₁₂-C₁₄ alcohol with 3 or 5 moles of ethylene oxide) 5 marketed by Hoechst. Preferred range of HLB in these products is from 8-11 and most preferred from 8-10.

Also useful as the nonionic surfactant of the surfactant 10 systems of the present invention are the alkylpolysaccharides disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, 15 e.g. a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl 20 moieties can be substituted for the glucosyl moieties (optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside). The intersaccharide bonds can be, e.g., between the one position of the 25 additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units.
The preferred alkylpolyglycosides have the formula



30

wherein R² is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon 35 atoms; n is 2 or 3, preferably 2; t is from 0 to about 10,

preferably 0; and x is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or 5 alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, 10 preferably predominately the 2-position.

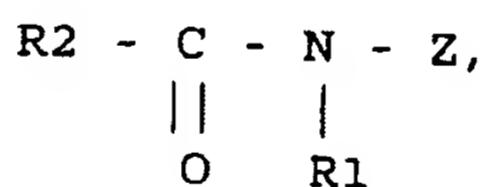
The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are also suitable for use as the 15 additional nonionic surfactant systems of the present invention. The hydrophobic portion of these compounds will preferably have a molecular weight of from about 1500 to about 1800 and will exhibit water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion 20 tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of 25 ethylene oxide. Examples of compounds of this type include certain of the commercially-available PlurafacTM LF404 and PluronicTM surfactants, marketed by BASF.

Also suitable for use as the nonionic surfactant of the 30 nonionic surfactant system of the present invention, are the condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and 35 excess propylene oxide, and generally has a molecular weight

of from about 2500 to about 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from 5 about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available TetronicTM compounds, marketed by BASF.

Preferred for use as the nonionic surfactant of the 10 surfactant systems of the present invention are polyethylene oxide condensates of alkyl phenols, condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide, alkylpolysaccharides, and mixtures thereof. Most preferred are C₈-C₁₄ alkyl phenol ethoxylates having from 3 to 15 ethoxy groups and C₈-C₁₈ alcohol ethoxylates (preferably C₁₀ avg.) having from 2 to 10 ethoxy groups, and mixtures thereof.

Highly preferred nonionic surfactants are polyhydroxy 20 fatty acid amide surfactants of the formula.

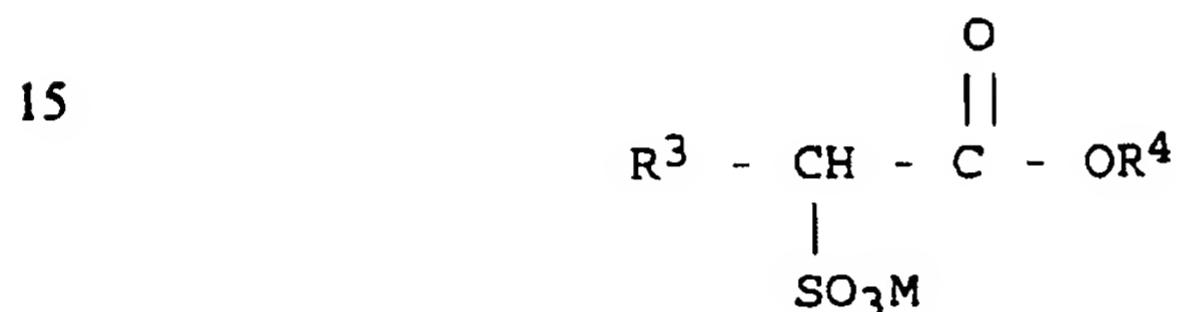


25

wherein R¹ is H, or R¹ is C₁₋₄ hydrocarbyl, 2-hydroxy ethyl, 30 2-hydroxy propyl or a mixture thereof, R² is C₅₋₃₁ hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof. Preferably, R¹ is methyl, R² is a straight C₁₁₋₁₅ alkyl or C₁₆₋₁₈ alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive 35 amination reaction.

Suitable anionic surfactants to be used are linear alkyl benzene sulfonate, alkyl ester sulfonate surfactants including linear esters of C₈-C₂₀ carboxylic acids (i.e., fatty acids) which are sulfonated with gaseous SO₃ according 5 to "The Journal of the American Oil Chemists Society", 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm oil, etc.

10 The preferred alkyl ester sulfonate surfactant, especially for laundry applications, comprise alkyl ester sulfonate surfactants of the structural formula :



20 wherein R³ is a C₈-C₂₀ hydrocarbyl, preferably an alkyl, or combination thereof, R⁴ is a C₁-C₆ hydrocarbyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with the alkyl ester sulfonate. Suitable salt-forming cations include metals such as sodium, 25 potassium, and lithium, and substituted or unsubstituted ammonium cations, such as monoethanolamine, diethanolamine, and triethanolamine. Preferably, R³ is C₁₀-C₁₆ alkyl, and R⁴ is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein R³ is C₁₀-C₁₆ alkyl.

30 Other suitable anionic surfactants include the alkyl sulfate surfactants which are water soluble salts or acids of the formula ROSO₃M wherein R preferably is a C₁₀-C₂₄ hydrocarbyl, preferably an alkyl or hydroxyalkyl having a 35 C₁₀-C₂₀ alkyl component, more preferably a C₁₂-C₁₈ alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal

cation (e.g. sodium, potassium, lithium), or ammonium or substituted ammonium (e.g. methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and 5 quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Typically, alkyl chains of C₁₂-C₁₆ are preferred for lower wash temperatures (e.g. below about 10 50°C) and C₁₆-18 alkyl chains are preferred for higher wash temperatures (e.g. above about 50°C).

Other anionic surfactants useful for detergents purposes can also be included in the cleaning compositions of the present invention. These can include salts (including, for 15 example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C₈-C₂₂ primary or secondary alkanesulfonates, C₈-C₂₄ olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline 20 earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C₈-C₂₄ alkylpolyglycolethersulfates (containing up to 10 moles of ethylene oxide); alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl 25 phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinates (especially saturated and unsaturated C₁₂-C₁₈ monoesters) and diesters 30 of sulfosuccinates (especially saturated and unsaturated C₆-C₁₂ diesters), acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, and alkyl 35 polyethoxy carboxylates such as those of the formula

RO(CH₂CH₂O)_k-CH₂COO-M⁺ wherein R is a C₈-C₂₂ alkyl, k is an integer from 1 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil.

Further examples are described in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

When included therein, the laundry detergent compositions of the present invention typically comprise from about 1% to about 40%, preferably from about 3% to about 20% by weight of such anionic surfactants.

Highly preferred anionic surfactants include alkyl alkoxylated sulfate surfactants hereof are water soluble salts or acids of the formula RO(A)_mSO₃M wherein R is an unsubstituted C₁₀-C₂₄ alkyl or hydroxyalkyl group having a C₁₀-C₂₄ alkyl component, preferably a C₁₂-C₂₀ alkyl or hydroxyalkyl, more preferably C₁₂-C₁₈ alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl, trimethyl-ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl

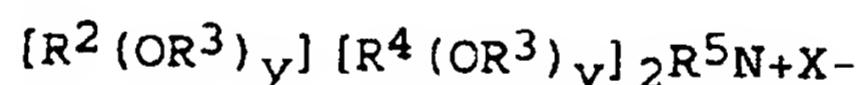
5 piperdinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C₁₂-C₁₈ alkyl polyethoxylate (1.0) sulfate (C₁₂-C₁₈E(1.0)M), C₁₂-C₁₈ alkyl polyethoxylate (2.25) sulfate (C₁₂-C₁₈E(2.25)M), C₁₂-C₁₈ alkyl polyethoxylate (3.0) sulfate (C₁₂-C₁₈E(3.0)M), and C₁₂-C₁₈ alkyl polyethoxylate (4.0) sulfate (C₁₂-C₁₈E(4.0)M), wherein M is conveniently selected from sodium and potassium.

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15 The cleaning compositions of the present invention may also contain cationic, amphoteric, zwitterionic, and semi-polar surfactants, as well as the nonionic and/or anionic surfactants other than those already described herein.

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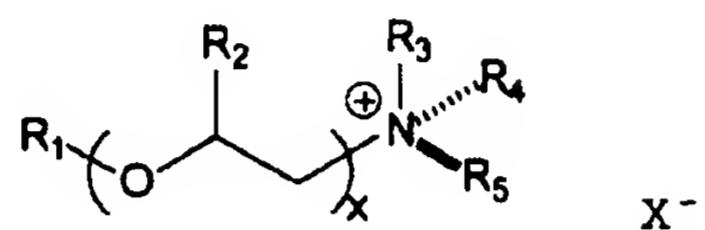
20 Cationic detergents suitable for use in the cleaning compositions of the present invention are those having one long-chain hydrocarbyl group. Examples of such cationic surfactants include the ammonium surfactants such as alkyltrimethylammonium halogenides, and those surfactants having the formula :



25 wherein R² is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each R³ is selected from the group consisting of -CH₂CH₂-, -CH₂CH(CH₃)-, -CH₂CH(CH₂OH)-, -CH₂CH₂CH₂-, and mixtures thereof; each R⁴ is selected from the group consisting of C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, benzyl ring structures formed by joining the two R⁴ groups, -CH₂CHOH-CHOHCOR⁶CHOHCH₂OH wherein R⁶ is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0; R⁵ is the same as R⁴ or is an alkyl chain wherein the total number of carbon atoms of R² plus R⁵ is not more than about 18; each y is from 0 to about 10 and the

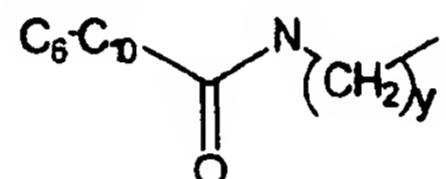
sum of the y values is from 0 to about 15; and X is any compatible anion.

Quaternary ammonium surfactant suitable for the present
5 invention has the formula (I) :



Formula I

whereby R₁ is a short chainlength alkyl (C₆-C₁₀) or
10 alkylamidoalkyl of the formula (II) :

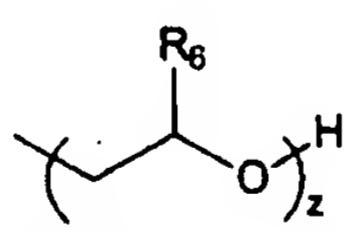


Formula II

y is 2-4, preferably 3.

15 whereby R₂ is H or a C₁-C₃ alkyl,
whereby x is 0-4, preferably 0-2, most preferably 0,
whereby R₃, R₄ and R₅ are either the same or different and
can be either a short chain alkyl (C₁-C₃) or alkoxylated
alkyl of the formula III,

20 whereby X⁻ is a counterion, preferably a halide, e.g.
chloride or methylsulfate.



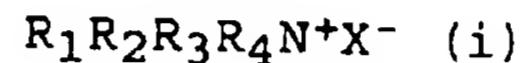
Formula III

25 R₆ is C₁-C₄ and z is 1 or 2.

Preferred quat ammonium surfactants are those as defined
in formula I whereby
R₁ is C₈, C₁₀ or mixtures thereof, x=0,

$R_3, R_4 = CH_3$ and $R_5 = CH_2CH_2OH$.

5 Highly preferred cationic surfactants are the water-soluble quaternary ammonium compounds useful in the present composition having the formula :



10 wherein R_1 is C_8-C_{16} alkyl, each of R_2 , R_3 and R_4 is independently C_1-C_4 alkyl, C_1-C_4 hydroxy alkyl, benzyl, and $-(C_2H_4O)_xH$ where x has a value from 2 to 5, and X is an anion. Not more than one of R_2 , R_3 or R_4 should be benzyl. The preferred alkyl chain length for R_1 is $C_{12}-C_{15}$ particularly where the alkyl group is a mixture of chain lengths derived from coconut or palm kernel fat or is 15 derived synthetically by olefin build up or OXO alcohols synthesis. Preferred groups for R_2R_3 and R_4 are methyl and hydroxyethyl groups and the anion X may be selected from halide, methosulfate, acetate and phosphate ions.

20 Examples of suitable quaternary ammonium compounds of formulae (i) for use herein are :

coconut trimethyl ammonium chloride or bromide;

coconut methyl dihydroxyethyl ammonium chloride or bromide;

25 decyl triethyl ammonium chloride;

decyl dimethyl hydroxyethyl ammonium chloride or bromide;

C_{12-15} dimethyl hydroxyethyl ammonium chloride or bromide;

coconut dimethyl hydroxyethyl ammonium chloride or bromide;

30 myristyl trimethyl ammonium methyl sulfate;

lauryl dimethyl benzyl ammonium chloride or bromide;

lauryl dimethyl (ethenoxy)₄ ammonium chloride or bromide;

choline esters (compounds of formula (i) wherein R_1 is

35 $CH_2-CH_2-O-C-C_{12-14}$ alkyl and $R_2R_3R_4$ are methyl).

||

O

di-alkyl imidazolines [compounds of formula (i)].

Other cationic surfactants useful herein are also described in U.S. Patent 4,228,044, Cambre, issued October 5 14, 1980 and in European Patent Application EP 000,224.

Typical cationic fabric softening components include the water-insoluble quaternary-ammonium fabric softening actives, the most commonly used having been di-long alkyl 10 chain ammonium chloride or methyl sulfate.

Preferred cationic softeners among these include the following:

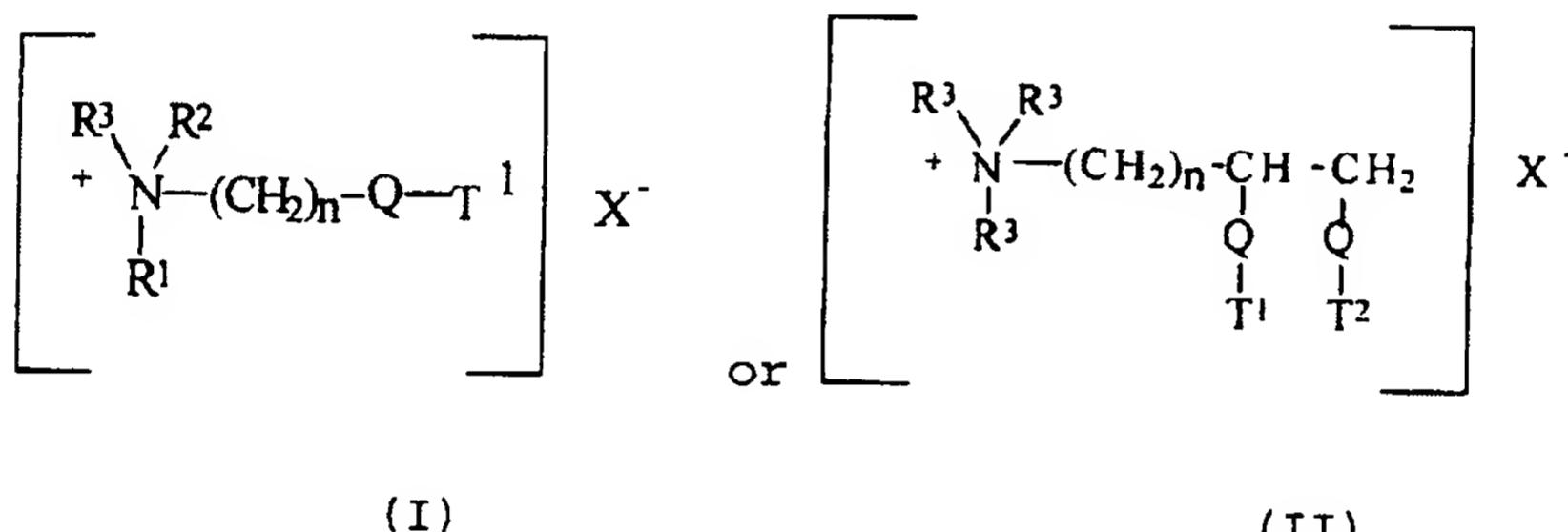
- 1) ditallow dimethylammonium chloride (DTDMAC);
- 2) dihydrogenated tallow dimethylammonium chloride;
- 15 3) dihydrogenated tallow dimethylammonium methylsulfate;
- 4) distearyl dimethylammonium chloride;
- 5) dioleyl dimethylammonium chloride;
- 6) dipalmityl hydroxyethyl methylammonium chloride;
- 20 7) stearyl benzyl dimethylammonium chloride;
- 8) tallow trimethylammonium chloride;
- 9) hydrogenated tallow trimethylammonium chloride;
- 10) C₁₂-14 alkyl hydroxyethyl dimethylammonium chloride;
- 25 11) C₁₂-18 alkyl dihydroxyethyl methylammonium chloride;
- 12) di(stearoyloxyethyl) dimethylammonium chloride (DSOEDMAC);
- 13) di(tallowoyloxyethyl) dimethylammonium chloride;
- 30 14) ditallow imidazolinium methylsulfate;
- 15) 1-(2-tallowylamidoethyl)-2-tallowyl imidazolinium methylsulfate.

Biodegradable quaternary ammonium compounds have been 35 presented as alternatives to the traditionally used di-long

alkyl chain ammonium chlorides and methyl sulfates. Such quaternary ammonium compounds contain long chain alk(en)yl groups interrupted by functional groups such as carboxy groups. Said materials and fabric softening compositions containing them are disclosed in numerous publications such as EP-A-0,040,562, and EP-A-0,239,910.

The quaternary ammonium compounds and amine precursors herein have the formula (I) or (II), below :

10



(I)

(II)

15 wherein Q is selected from $-O-C(O)-$, $-C(O)-O-$, $-O-C(O)-O-$, $-NR^4-C(O)-$, $-C(O)-NR^4-$;
 R¹ is $(CH_2)_n-Q-T^2$ or T³;
 R² is $(CH_2)_m-Q-T^4$ or T⁵ or R³;
 R³ is C₁-C₄ alkyl or C₁-C₄ hydroxyalkyl or H;
 20 R⁴ is H or C₁-C₄ alkyl or C₁-C₄ hydroxyalkyl;
 T¹, T², T³, T⁴, T⁵ are independently C₁₁-C₂₂ alkyl or alkenyl;
 n and m are integers from 1 to 4; and
 X⁻ is a softener-compatible anion.

25

Non-limiting examples of softener-compatible anions include chloride or methyl sulfate.

30 The alkyl, or alkenyl, chain T¹, T², T³, T⁴, T⁵ must contain at least 11 carbon atoms, preferably at least 16 carbon atoms. The chain may be straight or branched.

Tallow is a convenient and inexpensive source of long chain alkyl and alkenyl material. The compounds wherein T¹, T², T³, T⁴, T⁵ represents the mixture of long chain materials typical for tallow are particularly preferred.

5 Specific examples of quaternary ammonium compounds suitable for use in the aqueous fabric softening compositions herein include :

- 10 1) N,N-di(tallowyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;
- 2) N,N-di(tallowyl-oxy-ethyl)-N-methyl, N-(2-hydroxyethyl) ammonium methyl sulfate;
- 3) N,N-di(2-tallowyl-oxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
- 15 4) N,N-di(2-tallowyl-oxy-ethylcarbonyl-oxy-ethyl)-N,N-dimethyl ammonium chloride;
- 5) N-(2-tallowyl-oxy-2-ethyl)-N-(2-tallowyl-oxy-2-oxo-ethyl)-N,N-dimethyl ammonium chloride;
- 20 6) N,N,N-tri(tallowyl-oxy-ethyl)-N-methyl ammonium chloride;
- 7) N-(2-tallowyl-oxy-2-oxo-ethyl)-N-(tallowyl-N,N-dimethyl- ammonium chloride; and
- 8) 1,2-ditallowyl-oxy-3-trimethylammoniopropane chloride;

25 and mixtures of any of the above materials.

30

When included therein, the cleaning compositions of the present invention typically comprise from 0.2% to about 25%, preferably from about 1% to about 8% by weight of such cationic surfactants.

35

Ampholytic surfactants are also suitable for use in the cleaning compositions of the present invention. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in

which the aliphatic radical can be straight- or branched-chain. One of the aliphatic substituents contains at least about 8 carbon atoms, typically from about 8 to about 18 carbon atoms, and at least one contains an anionic water-

5 solubilizing group, e.g. carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, lines 18-35, for examples of ampholytic surfactants.

10 When included therein, the cleaning compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such ampholytic surfactants.

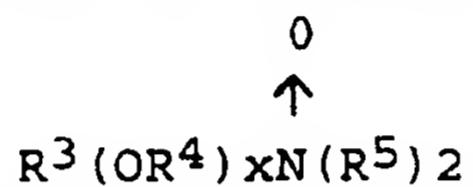
15 Zwitterionic surfactants are also suitable for use in cleaning compositions. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary 20 phosphonium or tertiary sulfonium compounds. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, line 38 through column 22, line 48, for examples of zwitterionic surfactants.

25 When included therein, the cleaning compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such zwitterionic surfactants.

30 Semi-polar nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups 35 containing from about 1 to about 3 carbon atoms; water-

soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and
5 water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

Semi-polar nonionic detergent surfactants include the amine
10 oxide surfactants having the formula



wherein R³ is an alkyl, hydroxyalkyl, or alkyl phenyl group
15 or mixtures therof containing from about 8 to about 22 carbon atoms; R⁴ is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof; x is from 0 to about 3; and each R⁵ is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon
20 atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The R⁵ groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

25 These amine oxide surfactants in particular include C₁₀-C₁₈ alkyl dimethyl amine oxides and C₈-C₁₂ alkoxy ethyl dihydroxy ethyl amine oxides.

When included therein, the cleaning compositions of the
30 present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such semi-polar nonionic surfactants.

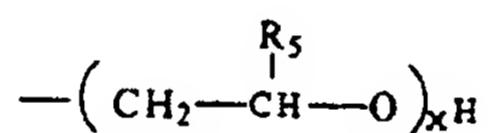
35 The cleaning composition of the present invention may further comprise a cosurfactant selected from the group of primary or tertiary amines. Suitable primary amines for use

herein include amines according to the formula R_1NH_2 wherein R_1 is a C₆-C₁₂, preferably C₆-C₁₀ alkyl chain or $R_4X(CH_2)_n$, X is -O-, -C(O)NH- or -NH-, R_4 is a C₆-C₁₂ alkyl chain n is between 1 to 5, preferably 3. R_1 alkyl chains may be straight or branched and may be interrupted with up to 12, preferably less than 5 ethylene oxide moieties.

Preferred amines according to the formula herein above are n-alkyl amines. Suitable amines for use herein may be selected from 1-hexylamine, 1-octylamine, 1-decylamine and laurylamine. Other preferred primary amines include C₈-C₁₀ oxypropylamine, octyloxypropylamine, 2-ethylhexyl-oxypropylamine, lauryl amido propylamine and amido propylamine.

15

Suitable tertiary amines for use herein include tertiary amines having the formula $R_1R_2R_3N$ wherein R_1 and R_2 are C₁-C₈ alkyl chains or

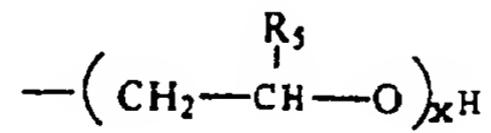


20 R_3 is either a C₆-C₁₂, preferably C₆-C₁₀ alkyl chain, or R_3 is $R_4X(CH_2)_n$, whereby X is -O-, -C(O)NH- or -NH-, R_4 is a C₄-C₁₂, n is between 1 to 5, preferably 2-3. R_5 is H or C₁-C₂ alkyl and x is between 1 to 6.

25 R_3 and R_4 may be linear or branched; R_3 alkyl chains may be interrupted with up to 12, preferably less than 5, ethylene oxide moieties.

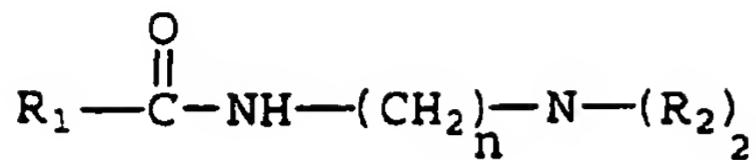
Preferred tertiary amines are $R_1R_2R_3N$ where R_1 is a C₆-C₁₂ alkyl chain, R_2 and R_3 are C₁-C₃ alkyl or

30



where R_5 is H or CH₃ and x = 1-2.

Also preferred are the amidoamines of the formula:



wherein R_1 is C_6-C_{12} alkyl; n is 2-4, preferably n is 3; R_2 and R_3 is C_1-C_4

5 Most preferred amines of the present invention include 1-octylamine, 1-hexylamine, 1-decylamine, 1-dodecylamine, C8-10oxypropylamine, N coco 1,3diaminopropane, coconutalkyldimethylamine, lauryldimethylamine, lauryl bis(hydroxyethyl)amine, coco bis(hydroxyethyl)amine, lauryl 10 amine 2 moles propoxylated, octyl amine 2 moles propoxylated, lauryl amidopropyldimethylamine, C8-10 amidopropyldimethylamine and C10 amidopropyldimethylamine. The most preferred amines for use in the compositions herein are 1-hexylamine, 1-octylamine, 1-decylamine, 1-dodecylamine. Especially desirable are n-dodecyldimethylamine and bishydroxyethylcoconutalkylamine and oleylamine 7 times ethoxylated, lauryl amido propylamine and cocoamido propylamine.

20 **Conventional detergent enzymes**

The cleaning compositions can in addition to mycodextranase enzyme further comprise one or more enzymes which provide cleaning performance and/or fabric care benefits.

25 Said enzymes include enzymes selected from cellulases, hemicellulases, peroxidases, proteases, gluco-amylases, amylases, xylanases, lipases, phospholipases, esterases, cutinases, pectinases, keratanases, reductases, oxidases, 30 phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, β -glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase or mixtures thereof.

A preferred combination is a cleaning composition having cocktail of conventional applicable enzymes like protease, amylase, lipase, cutinase and/or cellulase in conjunction with one or more plant cell wall degrading enzymes.

The cellulases usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgaard et al, which discloses fungal cellulase produced from *Humicola insolens*. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832.

15

Examples of such cellulases are cellulases produced by a strain of *Humicola insolens* (*Humicola grisea* var. *thermoidea*), particularly the *Humicola* strain DSM 1800. Other suitable cellulases are cellulases originated from *Humicola insolens* having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids; and a ~43kD endoglucanase derived from *Humicola insolens*, DSM 1800, exhibiting cellulase activity; a preferred endoglucanase component has the amino acid sequence disclosed in PCT Patent Application No. WO 91/17243. Also suitable cellulases are the EGIII cellulases from *Trichoderma longibrachiatum* described in WO94/21801, Genencor, published September 29, 1994. Especially suitable cellulases are the cellulases having color care benefits. Examples of such cellulases are cellulases described in European patent application No. 91202879.2, filed November 6, 1991 (Novo). Carezyme and Celluzyme (Novo Nordisk A/S) are especially useful. See also WO91/17243.

Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching", i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, WO89/09813 and in European Patent application EP No. 91202882.6, filed on November 6, 1991 and EP No. 96870013.8, filed February 20, 1996. Also suitable is the laccase enzyme.

15

Preferred enhancers are substituted phenothiazine and phenoxazine 10-Phenothiazinepropionic acid (PPT), 10-ethylphenothiazine-4-carboxylic acid (EPC), 10-phenoxazinepropionic acid (POP) and 10-methylphenoxazine (described in WO 94/12621) and substituted syringates (C3-C5 substituted alkyl syringates) and phenols. Sodium percarbonate or perborate are preferred sources of hydrogen peroxide.

25 Said cellulases and/or peroxidases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

30 Other preferred enzymes that can be included in the detergent compositions of the present invention include lipases. Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in 35 British Patent 1,372,034. Suitable lipases include those

which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescent IAM 1057*. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the 5 trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. 10 Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. Especially suitable lipases are lipases such as M1 Lipase^R and Lipomax^R (Gist-Brocades) and Lipolase^R and Lipolase Ultra^R (Novo) which have found to be very effective when used in combination with the 15 compositions of the present invention.

Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Addition of cutinases 20 to detergent compositions have been described in e.g. WO-A-88/09367 (Genencor).

The lipases and/or cutinases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of 25 active enzyme by weight of the detergent composition.

Suitable proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis* (subtilisin BPN and BPN'). One suitable 30 protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE[®] by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. 35 Other suitable proteases include ALCALASE[®], DURAZYM[®] and

SAVINASE[®] from Novo and MAXATASE[®], MAXACAL[®], PROPERASE[®] and MAXAPEM[®] (protein engineered Maxacal) from Gist-Brocades. Proteolytic enzymes also encompass modified bacterial serine proteases, such as those described in European Patent Application Serial Number 87 303761.8, filed April 28, 1987 (particularly pages 17, 24 and 98), and which is called herein "Protease B", and in European Patent Application 199,404, Venegas, published October 29, 1986, which refers to a modified bacterial serine proteolytic enzyme which is called "Protease A" herein.

More preferred is what is called herein "Protease C", which is a variant of an alkaline serine protease from Bacillus in which lysine replaced arginine at position 27, tyrosine replaced valine at position 104, serine replaced asparagine at position 123, and alanine replaced threonine at position 274. Protease C is described in EP 90915958:4, corresponding to WO 91/06637, Published May 16, 1991. Genetically modified variants, particularly of Protease C, are also included herein. See also a high pH protease from Bacillus sp. NCIMB 40338 described in WO 93/18140 A to Novo.

Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 92/03529 A to Novo. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 95/07791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 94/25583 to Novo.

In more detail, protease referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid

for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group 5 consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in WO95/10591 and in the patent 10 application of C. Ghosh, et al, "Bleaching Compositions Comprising Protease Enzymes" having US Serial No. 08/322,677, filed October 13, 1994.

Also suitable for the present invention are proteases 15 described in patent applications EP 251 446 and WO91/06637 and protease BLAP[®] described in WO91/02792. The proteolytic enzymes are incorporated in the detergent compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.001% to 0.2%, more preferably from 0.005% 20 to 0.1% pure enzyme by weight of the composition.

Amylases (α and/or β) can be included for removal of carbohydrate-based stains. WO94/02597, Novo Nordisk A/S published February 03, 1994, describes cleaning compositions 25 which incorporate mutant amylases. See also WO94/18314, Genencor, published August 18, 1994 and WO95/10603, Novo Nordisk A/S, published April 20, 1995. Other amylases known for use in cleaning compositions include both α - and β -amylases. α -Amylases are known in the art and include 30 those disclosed in US Pat. no. 5,003,257; EP 252,666; WO/91/00353; FR 2,676,456; EP 285,123; EP 525,610; EP 368,341; and British Patent specification no. 1,296,839 (Novo). Other suitable amylase are stability-enhanced amylases including Purafact Ox Am[®] described in WO 94/18314, 35 published August 18, 1994 and WO96/05295, Genencor,

published Februaury 22, 1996 and amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S, disclosed in WO 95/10603, published April 95.

5

Examples of commercial α -amylases products are Termamyl[®], Ban[®], Fungamyl[®] and Duramyl[®], all available from Novo Nordisk A/S Denmark. WO95/26397 describes other suitable amylases : α -amylases characterised by having a specific 10 activity at least 25% higher than the specific activity of Termamyl[®] at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas[®] α -amylase activity assay. Other amylolytic enzymes with 15 improved properties with respect to the activity level and the combination of thermostability and a higher activity level are described in WO95/35382.

The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and 20 yeast origin.

Origin can further be mesophilic or extremophilic (psychrophilic, psychrotrophic, thermophilic, barophilic, alkalophilic, acidophilic, halophilic, etc.). Purified or 25 non-purified forms of these enzymes may be used. Also included by definition, are mutants of native enzymes. Mutants can be obtained e.g. by protein and/or genetic engineering, chemical and/or physical modifications of native enzymes. Common practice as well is the expression of 30 the enzyme via host organisms in which the genetic material responsible for the production of the enzyme has been cloned.

Said enzymes are normally incorporated in the detergent 35 composition at levels from 0.0001% to 2% of active enzyme by

weight of the detergent composition. The enzymes can be added as separate single ingredients (prills, granulates, stabilized liquids, etc... containing one enzyme) or as mixtures of two or more enzymes (e.g. cocranulates).

5

Other suitable detergent ingredients that can be added are enzyme oxidation scavengers which are described in Copending European Patent application 92870018.6 filed on January 31, 1992. Examples of such enzyme oxidation 10 scavengers are ethoxylated tetraethylene polyamines.

A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 9307263 A and WO 9307260 A to Genencor 15 International, WO 8908694 A to Novo, and U.S. 3,553,139, January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. 4,101,457, Place et al, July 18, 1978, and in U.S. 4,507,219, Hughes, March 26, 1985.

20 Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. 4,261,868, Hora et al, April 14, 1981. Enzymes for use in detergents can be stabilised by various techniques. Enzyme stabilisation 25 techniques are disclosed and exemplified in U.S. 3,600,319, August 17, 1971, Gedge et al, EP 199,405 and EP 200,586, October 29, 1986, Venegas. Enzyme stabilisation systems are also described, for example, in U.S. 3,519,570. A useful *Bacillus*, sp. AC13 giving proteases, xylanases and 30 cellulases, is described in WO 9401532 A to Novo.

Color care benefits

Technologies which provide a type of color care benefit can also be included. Examples of these technologies are 35 metallo catalysts for color maintenance. Such metallo

catalysts are described in copending European Patent Application No. 92870181.2.

Bleaching agent

5 Additional optional detergent ingredients that can be included in the cleaning compositions of the present invention include bleaching agents such as hydrogen peroxide, PB1, PB4 and percarbonate with a particle size of 400-800 microns. These bleaching agent components can 10 include one or more oxygen bleaching agents and, depending upon the bleaching agent chosen, one or more bleach activators. When present oxygen bleaching compounds will typically be present at levels of from about 1% to about 25%.

15 The bleaching agent component for use herein can be any of the bleaching agents useful for cleaning compositions including oxygen bleaches as well as others known in the art. The bleaching agent suitable for the present invention 20 can be an activated or non-activated bleaching agent.

One category of oxygen bleaching agent that can be used encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include 25 magnesium monoperoxyphthalate hexahydrate, the magnesium salt of meta-chloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, U.S. Patent Application 740,446, European Patent Application 30 0,133,354 and U.S. Patent 4,412,934. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxycaproic acid as described in U.S. Patent 4,634,551.

Another category of bleaching agents that can be used 35 encompasses the halogen bleaching agents. Examples of

hypohalite bleaching agents, for example, include trichloro isocyanuric acid and the sodium and potassium dichloroisocyanurates and N-chloro and N-bromo alkane sulphonamides. Such materials are normally added at 0.5-10% by weight of the finished product, preferably 1-5% by weight.

The hydrogen peroxide releasing agents can be used in combination with bleach activators such as tetraacetyl ethylenediamine (TAED), nonanoyloxybenzenesulfonate (NOBS, described in US 4,412,934), 3,5,-trimethylhexanoloxybenzenesulfonate (ISONOBS, described in EP 120,591) or pentaacetylglucose (PAG) or Phenolsulfonate ester of N-nanonoyl-6-aminocaproic acid (NACA-OBS, described in WO94/28106), which are perhydrolyzed to form a peracid as the active bleaching species, leading to improved bleaching effect. Also suitable activators are acylated citrate esters such as disclosed in Copending European Patent Application No. 91870207.7.

20

Useful bleaching agents, including peroxyacids and bleaching systems comprising bleach activators and peroxygen bleaching compounds for use in detergent compositions according to the invention are described in our co-pending applications USSN 08/136,626, PCT/US95/07823, WO95/27772, WO95/27773, WO95/27774 and WO95/27775.

The hydrogen peroxide may also be present by adding an enzymatic system (i.e. an enzyme and a substrate therefore) which is capable of generating hydrogen peroxide at the beginning or during the washing and/or rinsing process. Such enzymatic systems are disclosed in EP Patent Application 91202655.6 filed October 9, 1991.

Metal-containing catalysts for use in bleach compositions, include cobalt-containing catalysts such as Pentaamine acetate cobalt(III) salts and manganese-containing catalysts such as those described in EPA 549 271; 5 EPA 549 272; EPA 458 397; US 5,246,621; EPA 458 398; US 5,194,416 and US 5,114,611. Bleaching composition comprising a peroxy compound, a manganese-containing bleach catalyst and a chelating agent is described in the patent application No 94870206.3.

10

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the 15 sulfonated zinc and/or aluminum phthalocyanines. These materials can be deposited upon the substrate during the washing process. Upon irradiation with light, in the presence of oxygen, such as by hanging clothes out to dry in the daylight, the sulfonated zinc phthalocyanine is 20 activated and, consequently, the substrate is bleached. Preferred zinc phthalocyanine and a photoactivated bleaching process are described in U.S. Patent 4,033,718. Typically, detergent compositions will contain about 0.025% to about 25 1.25%, by weight, of sulfonated zinc phthalocyanine.

25

Builder system

The compositions according to the present invention may further comprise a builder system. Any conventional builder system is suitable for use herein including aluminosilicate 30 materials, silicates, polycarboxylates, alkyl- or alkenyl-succinic acid and fatty acids, materials such as ethylenediamine tetraacetate, diethylene triamine pentamethyleneacetate, metal ion sequestrants such as aminopolyphosphonates, particularly ethylenediamine 35 tetramethylene phosphonic acid and diethylene triamine

pentamethylenephosphonic acid. Phosphate builders can also be used herein.

5 Suitable builders can be an inorganic ion exchange material, commonly an inorganic hydrated aluminosilicate material, more particularly a hydrated synthetic zeolite such as hydrated zeolite A, X, B, HS or MAP.

10 Another suitable inorganic builder material is layered silicate, e.g. SKS-6 (Hoechst). SKS-6 is a crystalline layered silicate consisting of sodium silicate ($Na_2Si_2O_5$).

15 Suitable polycarboxylates containing one carboxy group include lactic acid, glycolic acid and ether derivatives thereof as disclosed in Belgian Patent Nos. 831,368, 821,369 and 821,370. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycollic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates described in German Offenlegenschrift 2,446,686, and 2,446,687 and U.S. Patent No. 3,935,257 and the sulfinyl carboxylates described in Belgian Patent No. 840,623. Polycarboxylates containing three carboxy groups include, in particular, water-soluble 20 citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane 25 tricarboxylates described in British Patent No. 1,387,447.

30 Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane 35 tetracarboxylates and 1,1,2,3-propane tetracarboxylates.

Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British 5 Patent No. 1,082,179, while polycarboxylates containing phosphone substituents are disclosed in British Patent No. 1,439,000.

Alicyclic and heterocyclic polycarboxylates include 10 cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5-tetrahydro-furan - cis, cis, cis-tetracarboxylates, 2,5-tetrahydro-furan -cis - dicarboxylates, 2,2,5,5-tetrahydrofuran -tetracarboxylates, 1,2,3,4,5,6-hexane -hexacarboxylates and 15 and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol and xylitol. Aromatic poly-carboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent No. 1,425,343. Of the above, the preferred polycarboxylates are 20 hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

Preferred builder systems for use in the present compositions include a mixture of a water-insoluble 25 aluminosilicate builder such as zeolite A or of a layered silicate (SKS-6), and a water-soluble carboxylate chelating agent such as citric acid.

A suitable chelant for inclusion in the detergent 30 compositions in accordance with the invention is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof. Preferred EDDS compounds are the free acid form and the sodium or magnesium 35 salt thereof. Examples of such preferred sodium salts of

EDDS include Na_2EDDS and Na_4EDDS . Examples of such preferred magnesium salts of EDDS include MgEDDS and Mg_2EDDS . The magnesium salts are the most preferred for inclusion in compositions in accordance with the invention.

5

Preferred builder systems include a mixture of a water-insoluble aluminosilicate builder such as zeolite A, and a watersoluble carboxylate chelating agent such as citric acid. Preferred builder systems for use in liquid detergent 10 compositions of the present invention are soaps and polycarboxylates.

Other builder materials that can form part of the builder system for use in granular compositions include 15 inorganic materials such as alkali metal carbonates, bicarbonates, silicates, and organic materials such as the organic phosphonates, amino polyalkylene phosphonates and amino polycarboxylates.

20 Other suitable water-soluble organic salts are the homo- or co-polymeric acids or their salts, in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of this type are disclosed in GB-A-1,596,756. 25 Examples of such salts are polyacrylates of MW 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 20,000 to 70,000, especially about 40,000.

30 Detergency builder salts are normally included in amounts of from 5% to 80% by weight of the composition preferably from 10% to 70% and most usually from 30% to 60% by weight.

35 Suds suppressor

Another optional ingredient is a suds suppressor, exemplified by silicones, and silica-silicone mixtures. Silicones can be generally represented by alkylated polysiloxane materials while silica is normally used in finely divided forms exemplified by silica aerogels and xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds suppressor is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent impermeable carrier. Alternatively the suds suppressor can be dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other components.

15 A preferred silicone suds controlling agent is disclosed in Bartollotta et al. U.S. Patent 3 933 672. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in German Patent Application DTOS 2 646 126 published April 28, 1977.

20 An example of such a compound is DC-544, commercially available from Dow Corning, which is a siloxane-glycol copolymer. Especially preferred suds controlling agent are the suds suppressor system comprising a mixture of silicone oils and 2-alkyl-alkanols. Suitable 2-alkyl-alkanols are 2-butyl-octanol which are commercially available under the trade name Isofol 12 R.

25 Such suds suppressor system are described in Copending European Patent application N 92870174.7 filed 10 November, 1992.

30

Especially preferred silicone suds controlling agents are described in Copending European Patent application N°92201649.8. Said compositions can comprise a silicone/silica mixture in combination with fumed nonporous silica such as Aerosil®.

The suds suppressors described above are normally employed at levels of from 0.001% to 2% by weight of the composition, preferably from 0.01% to 1% by weight.

5

Others

Other components used in cleaning compositions may be employed, such as soil-suspending agents, soil-release agents, optical brighteners, abrasives, bactericides, 10 tarnish inhibitors, coloring agents, and/or encapsulated or non-encapsulated perfumes.

Especially suitable encapsulating materials are water soluble capsules which consist of a matrix of polysaccharide 15 and polyhydroxy compounds such as described in GB 1,464,616.

Other suitable water soluble encapsulating materials comprise dextrins derived from ungelatinized starch acid-esters of substituted dicarboxylic acids such as described 20 in US 3,455,838. These acid-ester dextrins are, preferably, prepared from such starches as waxy maize, waxy sorghum, sago, tapioca and potato. Suitable examples of said encapsulating materials include N-Lok manufactured by National Starch. The N-Lok encapsulating material consists 25 of a modified maize starch and glucose. The starch is modified by adding monofunctional substituted groups such as octenyl succinic acid anhydride.

Antiredeposition and soil suspension agents suitable 30 herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts. Polymers of this type include the polyacrylates and maleic anhydride-acrylic acid 35 copolymers previously mentioned as builders, as well as

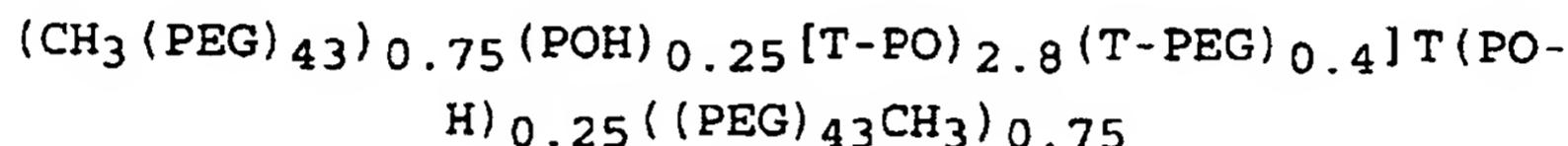
copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic anhydride constituting at least 20 mole percent of the copolymer. These materials are normally used at levels of from 0.5% to 10% by weight, 5 more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

Preferred optical brighteners are anionic in character, examples of which are disodium 4,4'-bis-(2-diethanolamino-4-10 anilino -s- triazin-6-ylamino)stilbene-2:2' disulphonate, disodium 4, - 4'-bis-(2-morpholino-4-anilino-s-triazin-6-ylamino-stilbene-2:2' - disulphonate, disodium 4,4' - bis-(2,4-dianilino-s-triazin-6-ylamino)stilbene-2:2' - disulphonate, monosodium 4',4'' -bis-(2,4-dianilino-s-tri-15 azin-6 ylamino)stilbene-2-sulphonate, disodium 4,4' -bis-(2-anilino-4- (N-methyl-N-2-hydroxyethylamino)-s-triazin-6-ylamino)stilbene-2,2' - disulphonate, di-sodium 4,4' -bis-(4-phenyl-2,1,3-triazol-2-yl)-stilbene-2,2' disulphonate, di-so-dium 4,4'bis(2-anilino-4-(1-methyl-2-20 hydroxyethylamino)-s-triazin-6- ylami-no)stilbene-2,2' disulphonate, sodium 2(stilbyl-4'''-(naphtho-1',2':4,5)-1,2,3 - triazole-2''-sulphonate and 4,4'-bis(2-sulphostyryl)biphenyl. Highly preferred brighteners are the specific brighteners of copending European Patent 25 application No. 95201943.8.

Other useful polymeric materials are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 30 4000. These are used at levels of from 0.20% to 5% more preferably from 0.25% to 2.5% by weight. These polymers and the previously mentioned homo- or co-polymeric polycarboxylate salts are valuable for improving whiteness maintenance, fabric ash deposition, and cleaning performance

on clay, proteinaceous and oxidizable soils in the presence of transition metal impurities.

Soil release agents useful in compositions of the present invention are conventionally copolymers or terpolymers of terephthalic acid with ethylene glycol and/or propylene glycol units in various arrangements. Examples of such polymers are disclosed in the commonly assigned US Patent Nos. 4116885 and 4711730 and European Published Patent Application No. 0 272 033. A particular preferred polymer in accordance with EP-A-0 272 033 has the formula



15

where PEG is $-\text{OC}_2\text{H}_4\text{O}-$, PO is $(\text{OC}_3\text{H}_6\text{O})$ and T is $(\text{pcOC}_6\text{H}_4\text{CO})$.

Also very useful are modified polyesters as random copolymers of dimethyl terephthalate, dimethyl sulfoisophthalate, ethylene glycol and 1-2 propane diol, the end groups consisting primarily of sulphobenzoate and secondarily of mono esters of ethylene glycol and/or propane-diol. The target is to obtain a polymer capped at both end by sulphobenzoate groups, "primarily", in the present context most of said copolymers herein will be end-capped by sulphobenzoate groups. However, some copolymers will be less than fully capped, and therefore their end groups may consist of monoester of ethylene glycol and/or propane 1-2 diol, thereof consist "secondarily" of such species.

The selected polyesters herein contain about 46% by weight of dimethyl terephthalic acid, about 16% by weight of propane 1-2 diol, about 10% by weight ethylene glycol about

13% by weight of dimethyl sulfobenzoic acid and about 15% by weight of sulfoisophthalic acid, and have a molecular weight of about 3,000. The polyesters and their method of preparation are described in detail in EPA 311 342.

5

Is is well known in the art that free chlorine in tap water rapidly deactivates the enzymes comprised in detergent compositions. Therefore, using chlorine scavenger such as perborate, ammonium sulfate, sodium sulphite or 10 polyethyleneimine at a level above 0.1% by weight of total composition, in the formulas will provide improved through the wash stability of the detergent enzymes. Compositions comprising chlorine scavenger are described in the European patent application 92870018.6 filed January 31, 1992.

15

Alkoxylated polycarboxylates such as those prepared from polyacrylates are useful herein to provide additional grease removal performance. Such materials are described in WO 91/08281 and PCT 90/01815 at p. 4 et seq., incorporated 20 herein by reference. Chemically, these materials comprise polyacrylates having one ethoxy side-chain per every 7-8 acrylate units. The side-chains are of the formula $-(\text{CH}_2\text{CH}_2\text{O})_m(\text{CH}_2)_n\text{CH}_3$ wherein m is 2-3 and n is 6-12. The side-chains are ester-linked to the polyacrylate "backbone" 25 to provide a "comb" polymer type structure. The molecular weight can vary, but is typically in the range of about 2000 to about 50,000. Such alkoxylated polycarboxylates can comprise from about 0.05% to about 10%, by weight, of the compositions herein.

30

Softening agents

Fabric softening agents can also be incorporated into laundry detergent compositions in accordance with the present invention. These agents may be inorganic or organic 35 in type. Inorganic softening agents are exemplified by the

smectite clays disclosed in GB-A-1 400 898 and in USP 5,019,292. Organic fabric softening agents include the water insoluble tertiary amines as disclosed in GB-A1 514 276 and EP-B0 011 340 and their combination with mono C12-5 C14 quaternary ammonium salts are disclosed in EP-B-0 026 527 and EP-B-0 026 528 and di-long-chain amides as disclosed in EP-B-0 242 919. Other useful organic ingredients of fabric softening systems include high molecular weight polyethylene oxide materials as disclosed in EP-A-0 299 575 10 and 0 313 146.

Levels of smectite clay are normally in the range from 2% to 20%, more preferably from 5% to 15% by weight, with the material being added as a dry mixed component to the 15 remainder of the formulation. Organic fabric softening agents such as the water-insoluble tertiary amines or dilong chain amide materials are incorporated at levels of from 0.5% to 5% by weight, normally from 1% to 3% by weight whilst the high molecular weight polyethylene oxide 20 materials and the water soluble cationic materials are added at levels of from 0.1% to 2%, normally from 0.15% to 1.5% by weight. These materials are normally added to the spray dried portion of the composition, although in some instances 25 it may be more convenient to add them as a dry mixed particulate, or spray them as molten liquid on to other solid components of the composition.

Dispersants

The cleaning composition of the present invention can 30 also contain dispersants : Suitable water-soluble organic salts are the homo- or co-polymeric acids or their salts, in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms.

Polymers of this type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MW 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 1,000 to 100,000.

5

Especially, copolymer of acrylate and methylacrylate such as the 480N having a molecular weight of 4000, at a level from 0.5-20% by weight of composition can be added in the cleaning compositions of the present invention.

10

The compositions of the invention may contain a lime soap peptiser compound, which has a lime soap dispersing power (LSDP), as defined hereinafter of no more than 8, preferably no more than 7, most preferably no more than 6. 15 The lime soap peptiser compound is preferably present at a level from 0% to 20% by weight.

A numerical measure of the effectiveness of a lime soap peptiser is given by the lime soap dispersant power (LSDP) 20 which is determined using the lime soap dispersant test as described in an article by H.C. Borghetty and C.A. Bergman, J. Am. Oil. Chem. Soc., volume 27, pages 88-90, (1950). This lime soap dispersion test method is widely used by practitioners in this art field being referred to, for example, in the following review articles; W.N. Linfield, Surfactant science Series, Volume 7, page 3; W.N. Linfield, Tenside surf. det., volume 27, pages 159-163, (1990); and M.K. Nagarajan, W.F. Masler, Cosmetics and Toiletries, volume 104, pages 71-73, (1989). The LSDP is the % weight 25 ratio of dispersing agent to sodium oleate required to disperse the lime soap deposits formed by 0.025g of sodium oleate in 30ml of water of 333ppm CaCO₃ (Ca:Mg=3:2) 30 equivalent hardness.

Surfactants having good lime soap peptiser capability will include certain amine oxides, betaines, sulfobetaines, alkyl ethoxysulfates and ethoxylated alcohols.

5 Exemplary surfactants having a LSDP of no more than 8 for use in accord with the present invention include C₁₆-C₁₈ dimethyl amine oxide, C₁₂-C₁₈ alkyl ethoxysulfates with an average degree of ethoxylation of from 1-5, particularly C₁₂-C₁₅ alkyl ethoxysulfate surfactant with a degree of ethoxylation of amount 3 (LSDP=4), and the C₁₄-C₁₅ ethoxylated alcohols with an average degree of ethoxylation of either 12 (LSDP=6) or 30, sold under the tradenames Lutensol A012 and Lutensol A030 respectively, by BASF GmbH.

10 15 Polymeric lime soap peptisers suitable for use herein are described in the article by M.K. Nagarajan, W.F. Masler, to be found in Cosmetics and Toiletries, volume 104, pages 71-73, (1989).

20 25 Hydrophobic bleaches such as 4-[N-octanoyl-6-aminohexanoyl]benzene sulfonate, 4-[N-nonanoyl-6-aminohexanoyl]benzene sulfonate, 4-[N-decanoyl-6-aminohexanoyl]benzene sulfonate and mixtures thereof; and nonanoyloxy benzene sulfonate together with hydrophilic / hydrophobic bleach formulations can also be used as lime soap peptisers compounds.

Dye transfer inhibition

30 The cleaning compositions of the present invention can also include compounds for inhibiting dye transfer from one fabric to another of solubilized and suspended dyes encountered during fabric laundering operations involving colored fabrics.

35 **Polymeric dye transfer inhibiting agents**

The cleaning compositions according to the present invention also comprise from 0.001% to 10 %, preferably from 0.01% to 2%, more preferably from 0.05% to 1% by weight of polymeric dye transfer inhibiting agents. Said polymeric dye transfer inhibiting agents are normally incorporated into cleaning compositions in order to inhibit the transfer of dyes from colored fabrics onto fabrics washed therewith. These polymers have the ability to complex or adsorb the fugitive dyes washed out of dyed fabrics before the dyes have the opportunity to become attached to other articles in the wash.

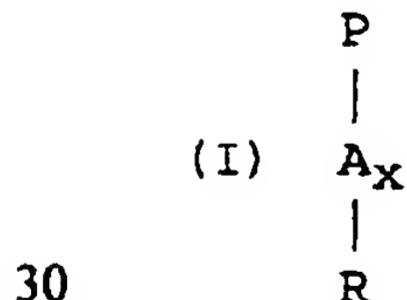
Especially suitable polymeric dye transfer inhibiting agents are polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers, polyvinyloxazolidones and polyvinylimidazoles or mixtures thereof.

Addition of such polymers also enhances the performance of the enzymes according the invention.

a) Polyamine N-oxide polymers

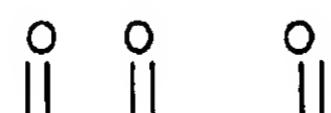
The polyamine N-oxide polymers suitable for use contain units having the following structure formula :

25



wherein P is a polymerisable unit, whereto the R-N-O group can be attached to or wherein the R-N-O group forms part of the polymerisable unit or a combination of both.

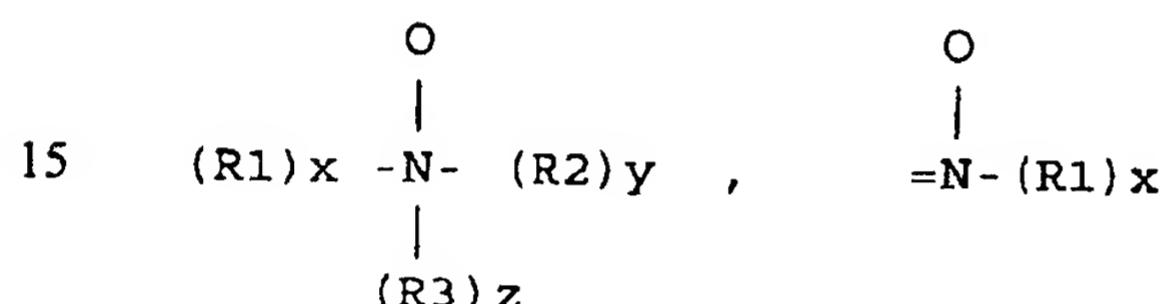
35



A is NC, CO, C, -O-, -S-, -N- ; x is 0 or 1;

5 R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

10 The N-O group can be represented by the following general structures :



20 wherein R1, R2, and R3 are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups.

25

The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

30 Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups.

35 One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine,

pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

Another class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group 5 is attached to the R-group.

Other suitable polyamine N-oxides are the polyamine oxides whereto the N-O group is attached to the polymerisable unit.

10

Preferred class of these polyamine N-oxides are the polyamine N-oxides having the general formula (I) wherein R is an aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is part of said R 15 group. Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyridine, pyrrole, imidazole and derivatives thereof.

Another preferred class of polyamine N-oxides are the 20 polyamine oxides having the general formula (I) wherein R are aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is attached to said R groups. Examples of these classes are polyamine oxides wherein R groups can be aromatic such as phenyl.

25

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, 30 polyethers, polyamide, polyimides, polyacrylates and mixtures thereof.

The amine N-oxide polymers of the present invention typically have a ratio of amine to the amine N-oxide of 10:1 35 to 1:1000000. However the amount of amine oxide groups

present in the polyamine oxide polymer can be varied by appropriate copolymerization or by appropriate degree of N-oxidation. Preferably, the ratio of amine to amine N-oxide is from 2:3 to 1:1000000. More preferably from 1:4 to 5 1:1000000, most preferably from 1:7 to 1:1000000. The polymers of the present invention actually encompass random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is either an amine N-oxide or not. The amine oxide unit of the polyamine N-oxides has a 10 $\text{PK}_a < 10$, preferably $\text{PK}_a < 7$, more preferred $\text{PK}_a < 6$. The polyamine oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power.

15

Typically, the average molecular weight is within the range of 500 to 1000,000; preferably from 1,000 to 50,000, more preferably from 2,000 to 30,000, most preferably from 3,000 to 20,000.

20

b) Copolymers of N-vinylpyrrolidone and N-vinylimidazole

The N-vinylimidazole N-vinylpyrrolidone polymers used in the present invention have an average molecular weight range from 5,000-1,000,000, preferably from 5,000-200,000.

25

Highly preferred polymers for use in detergent compositions according to the present invention comprise a polymer selected from N-vinylimidazole N-vinylpyrrolidone copolymers wherein said polymer has an average molecular 30 weight range from 5,000 to 50,000 more preferably from 8,000 to 30,000, most preferably from 10,000 to 20,000.

The average molecular weight range was determined by light scattering as described in Barth H.G. and Mays J.W. 35 Chemical Analysis Vol 113, "Modern Methods of Polymer

Characterization". Highly preferred N-vinylimidazole N-vinylpyrrolidone copolymers have an average molecular weight range from 5,000 to 50,000; more preferably from 8,000 to 30,000; most preferably from 10,000 to 20,000.

5

The N-vinylimidazole N-vinylpyrrolidone copolymers characterized by having said average molecular weight range provide excellent dye transfer inhibiting properties while not adversely affecting the cleaning performance of 10 detergent compositions formulated therewith.

The N-vinylimidazole N-vinylpyrrolidone copolymer of the present invention has a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2, more preferably from 0.8 15 to 0.3, most preferably from 0.6 to 0.4 .

c) Polyvinylpyrrolidone

The detergent compositions of the present invention may also utilize polyvinylpyrrolidone ("PVP") having an average 20 molecular weight of from about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000. Suitable polyvinylpyrrolidones are commercially available from ISP 25 Corporation, New York, NY and Montreal, Canada under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). Other suitable 30 polyvinylpyrrolidones which are commercially available from BASF Cooperation include Sokalan HP 165 and Sokalan HP 12; polyvinylpyrrolidones known to persons skilled in the detergent field (see for example EP-A-262,897 and EP-A-256,696).

d) Polyvinyloxazolidone :

The detergent compositions of the present invention may also utilize polyvinyloxazolidone as a polymeric dye transfer inhibiting agent. Said polyvinyloxazolidones have 5 an average molecular weight of from about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000.

10 e) Polyvinylimidazole :

The detergent compositions of the present invention may also utilize polyvinylimidazole as polymeric dye transfer inhibiting agent. Said polyvinylimidazoles have an average 15 about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000.

20 f) Cross-linked polymers :

Cross-linked polymers are polymers whose backbone are interconnected to a certain degree; these links can be of chemical or physical nature, possibly with active groups in the backbone or on branches; cross-linked polymers have been 25 described in the Journal of Polymer Science, volume 22, pages 1035-1039.

In one embodiment, the cross-linked polymers are made in such a way that they form a three-dimensional rigid 30 structure, which can entrap dyes in the pores formed by the three-dimensional structure. In another embodiment, the cross-linked polymers entrap the dyes by swelling.

Such cross-linked polymers are described in the co- 35 pending patent application 94870213.9

Method of washing

The compositions of the invention may be used in essentially any washing or cleaning methods, including 5 soaking methods, pretreatment methods and methods with rinsing steps for which a separate rinse aid composition may be added.

The process described herein comprises contacting 10 fabrics with a laundering solution in the usual manner and exemplified hereunder.

The process of the invention is conveniently carried out in the course of the cleaning process. The method of 15 cleaning is preferably carried out at 5°C to 95°C, especially between 10°C and 60°C. The pH of the treatment solution is preferably from 7 to 11.

A preferred machine dishwashing method comprises 20 treating soiled articles with an aqueous liquid having dissolved or dispensed therein an effective amount of the machine diswashing or rinsing composition. A conventional effective amount of the machine dishwashing composition means from 8-60 g of product dissolved or dispersed in a 25 wash volume from 3-10 litres.

According to a manual dishwashing method, soiled dishes are contacted with an effective amount of the diswashing composition, typically from 0.5-20g (per 25 dishes being 30 treated). Preferred manual dishwashing methods include the application of a concentrated solution to the surfaces of the dishes or the soaking in large volume of dilute solution of the detergent composition.

The following examples are meant to exemplify compositions of the present invention, but are not necessarily meant to limit or otherwise define the scope of the invention.

5

In the detergent compositions, the enzymes levels are expressed by pure enzyme by weight percentage of the total composition and the detergent ingredients are expressed by weight percentage of the total compositions, unless 10 otherwise specified. The abbreviated component identifications therein have the following meanings:

LAS : Sodium linear C_{12} alkyl benzene sulphonate

TAS : Sodium tallow alkyl sulfate

$C_{XY}AS$: Sodium C_{1X} - C_{1Y} alkyl sulfate

$C_{25}E_Y$: A C_{12} - C_{15} predominantly linear primary alcohol condensed with an average of Y moles of ethylene oxide

$C_{XY}E_Z$: A C_{1X} - C_{1Y} predominantly linear primary alcohol condensed with an average of Z moles of ethylene oxide

$C_{XY}E_ZS$: C_{1X} - C_{1Y} sodium alkyl sulfate condensed with an average of Z moles of ethylene oxide per mole

QAS : $R_2.N^+(CH_3)_2(C_2H_4OH)$ with $R_2 = C_{12}$ - C_{14}

Soap : Sodium linear alkyl carboxylate derived from a 80/20 mixture of tallow and coconut oils.

Nonionic : C₁₃-C₁₅ mixed ethoxylated/propoxylated fatty alcohol with an average degree of ethoxylation of 3.8 and an average degree of propoxylation of 4.5 sold under the tradename Plurafac LF404 by BASF GmbH.

CFAA : C₁₂-C₁₄ alkyl N-methyl glucamide

TFAA : C₁₆-C₁₈ alkyl N-methyl glucamide.

TPKFA : C₁₂-C₁₄ topped whole cut fatty acids.

DEQA : Di-(tallow-oxy-ethyl) dimethyl ammonium chloride.

SDASA : 1:2 ratio of stearyldimethyl amine:triple-pressed stearic acid.

Neodol 45-13 : C₁₄-C₁₅ linear primary alcohol ethoxylate, sold by Shell Chemical CO.

Tallow : Dihydrogenated tallowamidoethyl hydroxyethylmonium methosulfate / glycol distearate / cetyl alcohol.

Silicate : Amorphous Sodium Silicate (SiO₂:Na₂O ratio = 2.0)

NaSKS-6 : Crystalline layered silicate of formula δ -Na₂Si₂O₅.

Carbonate : Anhydrous sodium carbonate with a particle size between 200 μm and 900 μm .

Bicarbonate : Anhydrous sodium bicarbonate with a particle size between 400 μm and 1200 μm .

STPP : Anhydrous sodium tripolyphosphate

MA/AA : Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 80,000

PA30 : Polyacrylic acid of average molecular weight of approximately 8,000.

Terpolymer : Terpolymer of average molecular weight approx. 7,000, comprising acrylic:maleic:ethylacrylic acid monomer units at a weight ratio of 60:20:20

480N : Random copolymer of 3:7 acrylic/methacrylic acid, average molecular weight about 3,500.

Polyacrylate : Polyacrylate homopolymer with an average molecular weight of 8,000 sold under the tradename PA30 by BASF GmbH

Zeolite A : Hydrated Sodium Aluminosilicate of formula $\text{Na}_{12}(\text{AlO}_2\text{SiO}_2)_{12} \cdot 27\text{H}_2\text{O}$ having a primary particle size in the range from 0.1 to 10 micrometers

Citrate	: Tri-sodium citrate dihydrate of activity 86,4% with a particle size distribution between 425 μm and 850 μm .
Citric	: Anhydrous citric acid
PB1	: Anhydrous sodium perborate monohydrate bleach, empirical formula $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$
PB4	: Anhydrous sodium perborate tetrahydrate
Percarbonate	: Anhydrous sodium percarbonate bleach of empirical formula $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$
TAED	: Tetraacetyl ethylene diamine.
NOBS	: Nonanoyloxybenzene sulfonate in the form of the sodium salt.
Photoactivated Bleach	: Sulfonated zinc phtlocyanine encapsulated in dextrin soluble polymer.
PAAC	: Pentaamine acetate cobalt(III) salt.
Paraffin	: Paraffin oil sold under the tradename Winog 70 by Wintershall.
BzP	: Benzoyl Peroxide.
Mycodextranase	: 1,3-1,4-alpha-D-Glucan 4-glucanohydrolase

Protease : Proteolytic enzyme sold under the tradename Savinase, Alcalase, Durazym by Novo Nordisk A/S, Maxacal, Maxapem sold by Gist-Brocades and proteases described in patents WO91/06637 and/or WO95/10591 and/or EP 251 446.

Amylase : Amylolytic enzyme sold under the tradename Purafact Ox Am® described in WO 94/18314, WO96/05295 sold by Genencor; Termamyl®, Fungamyl® and Duramyl®. all available from Novo Nordisk A/S and those described in WO95/26397.

Lipase : Lipolytic enzyme sold under the tradename Lipolase, Lipolase Ultra by Novo Nordisk A/S

Cellulase : Cellulytic enzyme sold under the tradename Carezyme, Celluzyme and/or Endolase by Novo Nordisk A/S.

CMC : Sodium carboxymethyl cellulose.

HEDP : 1,1-hydroxyethane diphosphonic acid.

DETPMP : Diethylene triamine penta (methylene phosphonic acid), marketed by Monsanto under the Trade name Dequest 2060.

PVNO : Poly(4-vinylpyridine)-N-Oxide.

PVPVI : Poly (4-vinylpyridine)-N-oxide/copolymer of vinyl-imidazole and vinyl-pyrrolidone.

Brightener 1 : Disodium 4,4'-bis(2-sulphostyryl)biphenyl.

Brightener 2 : Disodium 4,4'-bis(4-anilino-6-morpholino-1,3,5-triazin-2-yl) stilbene-2:2'-disulfonate.

Silicone antifoam : Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1.

Granular Suds Suppressor : 12% Silicone/silica, 18% stearyl alcohol, 70% starch in granular form

SRP 1 : Sulfobenzoyl end capped esters with oxyethylene oxy and terephthaloyl backbone.

SRP 2 : Diethoxylated poly (1,2 propylene terephthalate) short block polymer.

SCS : Sodium cumene sulphonate

Sulfate : Anhydrous sodium sulfate.

HMWPEO : High molecular weight polyethylene oxide

PEG : Polyethylene glycol.

BTA : Benzotriazole

Bismuth nitrate : Bismuth nitrate salt

NaDCC : Sodium dichloroisocyanurate

Encapsulated perfume particles : Insoluble fragrance delivery technology utilising zeolite 13x, perfume and a dextrose/glycerin agglomerating binder.

KOH : 100% Active solution of Potassium Hydroxide

Silica dental abrasive : Precipitated silica identified as Zeodent 119 offered by J.M. Huber.

Carboxyvinyl polymer : Carbopol offered by B.F. Goodrich Chemical Company.

Carrageenan : Iota Carrageenan offered by Hercules Chemical Company.

pH : Measured as a 1% solution in distilled water at 20°C.

Example 1

The following laundry detergent compositions were prepared in accord with the invention:

5

	I	II	III	IV	V	VI
LAS	8.0	8.0	8.0	8.0	8.0	8.0
C25E3	3.4	3.4	3.4	3.4	3.4	3.4
QAS	-	0.8	0.8	-	0.8	0.8
Zeolite A	18.1	18.1	18.1	18.1	18.1	18.1
Carbonate	13.0	13.0	13.0	27.0	27.0	27.0
Silicate	1.4	1.4	1.4	3.0	3.0	3.0
Sulfate	26.1	26.1	26.1	26.1	26.1	26.1
PB4	9.0	9.0	9.0	9.0	9.0	9.0
TAED	1.5	1.5	1.5	1.5	1.5	1.5
DETPMP	0.25	0.25	0.25	0.25	0.25	0.25
HEDP	0.3	0.3	0.3	0.3	0.3	0.3
Mycodextranase	0.001	0.001	0.003	0.001	0.001	0.003
Protease	0.0026	0.0026	0.0026	0.0026	0.0026	0.0026
Amylase	-	0.0009	0.0009	0.0009	0.0009	0.0009
MA/AA	0.3	0.3	0.3	0.3	0.3	0.3
CMC	0.2	0.2	0.2	0.2	0.2	0.2
Photoactivated bleach (ppm)	15	15	15	15	15	15
Brightener 1	0.09	0.09	0.09	0.09	0.09	0.09
Perfume	0.3	0.3	0.3	0.3	0.3	0.3
Silicone antifoam	0.5	0.5	0.5	0.5	0.5	0.5
Misc/minors to 100%						
Density in g/litre	850	850	850	850	850	850

Example 2

5 The following granular laundry detergent compositions of bulk density 750 g/litre were prepared in accord with the invention:

	I	II	III
LAS	5.25	5.61	4.76
TAS	1.25	1.86	1.57
C45AS	-	2.24	3.89
C25AE3S	-	0.76	1.18
C45E7	3.25	-	5.0
C25E3	-	5.5	-
QAS	0.8	2.0	2.0
STPP	19.7	-	-
Zeolite A	-	19.5	19.5
NaSKS-6/citric acid (79:21)	-	10.6	10.6
Carbonate	6.1	21.4	21.4
Bicarbonate	-	2.0	2.0
Silicate	6.8	-	-
Sodium sulfate	39.8	-	14.3
PB4	5.0	12.7	-
TAED	0.5	3.1	-
DETPMP	0.25	0.2	0.2
HEDP	-	0.3	0.3
Mycodextranase	0.001	0.001	0.001
Protease	0.0026	0.0085	0.045
Lipase	0.003	0.003	0.003
Cellulase	0.0006	0.0006	0.0006
Amylase	0.0009	0.0009	0.0009
MA/AA	0.8	1.6	1.6
CMC	0.2	0.4	0.4
Photoactivated bleach (ppm)	15 ppm	27 ppm	27 ppm
Brightener 1	0.08	0.19	0.19
Brightener 2	-	0.04	0.04
Encapsulated perfume particles	0.3	0.3	0.3
Silicone antifoam	0.5	2.4	2.4
Minors/misc to 100%			

Example 3

5 The following detergent formulations, according to the present invention were prepared, where I is a phosphorus-containing detergent composition, II is a zeolite-containing detergent composition and III is a compact detergent composition:

	I	II	III
Blown Powder			
STPP	24.0	-	24.0
Zeolite A	-	24.0	-
C45AS	9.0	6.0	13.0
MA/AA	2.0	4.0	2.0
LAS	6.0	8.0	11.0
TAS	2.0	-	-
Silicate	7.0	3.0	3.0
CMC	1.0	1.0	0.5
Brightener 2	0.2	0.2	0.2
Soap	1.0	1.0	1.0
DETPMP	0.4	0.4	0.2
Spray On			
C45E7	2.5	2.5	2.0
C25E3	2.5	2.5	2.0
Silicone antifoam	0.3	0.3	0.3
Perfume	0.3	0.3	0.3
Dry additives			
Carbonate	6.0	13.0	15.0
PB4	18.0	18.0	10.0
PB1	4.0	4.0	0
TAED	3.0	3.0	1.0
Photoactivated bleach	0.02	0.02	0.02
Mycodextranase	0.001	0.001	0.001
Protease	0.01	0.01	0.01
Lipase	0.009	0.009	0.009
Amylase	0.002	0.003	0.001
Dry mixed sodium sulfate	3.0	3.0	5.0
Balance (Moisture & Miscellaneous)	100.0	100.0	100.0
Density (g/litre)	630	670	670

Example 4

The following nil bleach-containing detergent formulations of particular use in the washing of colored clothing, 5 according to the present invention were prepared:

	I	II	III
Blown Powder			
Zeolite A	15.0	15.0	-
Sodium sulfate	0.0	5.0	-
LAS	3.0	3.0	-
DETPMP	0.4	0.5	-
CMC	0.4	0.4	-
MA/AA	4.0	4.0	-
Agglomerates			
C45AS	-	-	11.0
LAS	6.0	5.0	-
TAS	3.0	2.0	-
Silicate	4.0	4.0	-
Zeolite A	10.0	15.0	13.0
CMC	-	-	0.5
MA/AA	-	-	2.0
Carbonate	9.0	7.0	7.0
Spray On			
Perfume	0.3	0.3	0.5
C45E7	4.0	4.0	4.0
C25E3	2.0	2.0	2.0
Dry additives			
MA/AA	-	-	3.0
NaSKS-6	-	-	12.0
Citrate	10.0	-	8.0
Bicarbonate	7.0	3.0	5.0
Carbonate	8.0	5.0	7.0
PVPVI/PVNO	0.5	0.5	0.5
Mycodextranase	0.1	0.1	0.1
Protease	0.026	0.016	0.047
Lipase	0.009	0.009	0.009
Amylase	0.005	0.005	0.005
Cellulase	0.006	0.006	0.006
Silicone antifoam	5.0	5.0	5.0
Dry additives			
Sodium sulfate	0.0	9.0	0.0
Balance (Moisture and Miscellaneous)	100.0	100.0	100.0

Density (g/litre)	700	700	700
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Example 5

The following detergent formulations, according to the present invention were prepared:

5

	I	II	III	IV
LAS	20.0	14.0	24.0	22.0
QAS	0.7	1.0	-	0.7
TFAA	-	1.0	-	-
C25E5/C45E7	-	2.0	-	0.5
C45E3S	-	2.5	-	-
STPP	30.0	18.0	30.0	22.0
Silicate	9.0	5.0	10.0	8.0
Carbonate	13.0	7.5	-	5.0
Bicarbonate	-	7.5	-	-
DETPMP	0.7	1.0	-	-
SRP 1	0.3	0.2	-	0.1
MA/AA	2.0	1.5	2.0	1.0
CMC	0.8	0.4	0.4	0.2
Mycodextranase	0.001	0.001	0.003	0.003
Protease	0.008	0.01	0.026	0.026
Amylase	0.007	0.004	-	0.002
Lipase	0.004	0.002	0.004	0.002
Cellulase	0.0015	0.0005	-	-
Photoactivated bleach (ppm)	70ppm	45ppm	-	10ppm
Brightener 1	0.2	0.2	0.08	0.2
PB1	6.0	2.0	-	-
NOBS	2.0	1.0	-	-
Balance (Moisture and Miscellaneous)	100	100	100	100

Example 6

The following detergent formulations, according to the present invention were prepared:

5

	I	II	III	IV
Blown Powder				
Zeolite A	30.0	22.0	6.0	6.7
Na SkS-6	-	-	-	3.3
Polycarboxylate	-	-	-	7.1
Sodium sulfate	19.0	5.0	7.0	-
MA/AA	3.0	3.0	6.0	-
LAS	14.0	12.0	22.0	21.5
C45AS	8.0	7.0	7.0	5.5
Cationic	-	-	-	1.0
Silicate	-	1.0	5.0	11.4
Soap	-	-	2.0	-
Brightener 1	0.2	0.2	0.2	-
Carbonate	8.0	16.0	20.0	10.0
DETPMP	-	0.4	0.4	-
Spray On				
C45E7	1.0	1.0	1.0	3.2
Dry additives				
PVPVI/PVNO	0.5	0.5	0.5	-
Mycodextranase	0.07	0.1	0.07	0.1
Protease	0.052	0.01	0.01	0.01
Lipase	0.009	0.009	0.009	0.009
Amylase	0.001	0.001	0.001	0.001
Cellulase	0.0002	0.0002	0.0002	0.0002
NOBS	-	6.1	4.5	3.2
PB1	1.0	5.0	6.0	3.9
Sodium sulfate	-	6.0	-	to balance
Balance (Moisture and Miscellaneous)	100	100	100	

Example 7

The following high density and bleach-containing detergent formulations, according to the present invention were
5 prepared:

	I	II	III
Blown Powder			
Zeolite A	15.0	15.0	15.0
Sodium sulfate	0.0	5.0	0.0
LAS	3.0	3.0	3.0
QAS	-	1.5	1.5
DETPMP	0.4	0.4	0.4
CMC	0.4	0.4	0.4
MA/AA	4.0	2.0	2.0
Agglomerates			
LAS	5.0	5.0	5.0
TAS	2.0	2.0	1.0
Silicate	3.0	3.0	4.0
Zeolite A	8.0	8.0	8.0
Carbonate	8.0	8.0	4.0
Spray On			
Perfume	0.3	0.3	0.3
C45E7	2.0	2.0	2.0
C25E3	2.0	-	-
Dry additives			
Citrate	5.0	-	2.0
Bicarbonate	-	3.0	-
Carbonate	8.0	15.0	10.0
TAED	6.0	2.0	5.0
PB1	14.0	7.0	10.0
Polyethylene oxide of MW			
5,000,000	-	-	0.2
Bentonite clay	-	-	10.0
Mycodextranase	0.001	0.001	0.001
Protease	0.01	0.01	0.01
Lipase	0.009	0.009	0.009
Amylase	0.005	0.005	0.005
Cellulase	0.002	0.002	0.002
Silicone antifoam	5.0	5.0	5.0
Dry additives			
Sodium sulfate	0.0	3.0	0.0

Balance (Moisture and Miscellaneous)	100.0	100.0	100.0
Density (g/litre)	850	850	850

Example 8

The following high density detergent formulations, according to the present invention were prepared:

5

	I	II
Agglomerate		
C45AS	11.0	14.0
Zeolite A	15.0	6.0
Carbonate	4.0	8.0
MA/AA	4.0	2.0
CMC	0.5	0.5
DETPMP	0.4	0.4
Spray On		
C25E5	5.0	5.0
Perfume	0.5	0.5
Dry Adds		
HEDP	0.5	0.3
SKS 6	13.0	10.0
Citrate	3.0	1.0
TAED	5.0	7.0
Percarbonate	20.0	20.0
SRP 1	0.3	0.3
Mycodextranase	0.001	0.003
Protease	0.014	0.014
Lipase	0.009	0.009
Cellulase	0.001	0.001
Amylase	0.005	0.005
Silicone antifoam	5.0	5.0
Brightener 1	0.2	0.2
Brightener 2	0.2	-
Balance (Moisture and Miscellaneous)	100	100
Density (g/litre)	850	850

Example 9

The following granular detergent formulations, according to the present invention were prepared:

5

	I	II	III	IV	V
LAS	21.0	25.0	18.0	18.0	-
Coco C12-14 AS	-	-	-	-	21.9
AE3S	-	-	1.5	1.5	2.3
Decyl dimethyl hydroxyethyl NH4+Cl	-	0.4	0.7	0.7	0.8
Nonionic	1.2	-	0.9	0.5	-
Coco C12-14 Fatty	-	-	-	-	1.0
Alcohol					
STPP	44.0	25.0	22.5	22.5	22.5
Zeolite A	7.0	10.0	-	-	8.0
MA/AA	-	-	0.9	0.9	-
SRP1	0.3	0.15	0.2	0.1	0.2
CMC	0.3	2.0	0.75	0.4	1.0
Carbonate	17.5	29.3	5.0	13.0	15.0
Silicate	2.0	-	7.6	7.9	-
Mycodextranase	0.003	0.001	0.001	0.003	0.003
Protease	0.007	0.007	0.007	0.007	0.007
Amylase	-	0.004	0.004	0.004	0.004
Lipase	0.003	0.003	0.003	-	-
Cellulase	-	0.001	0.001	0.001	0.001
NOBS	-	-	-	1.2	1.0
PB1	-	-	-	2.4	1.2
Diethylene triamine penta acetic acid	-	-	-	0.7	1.0
Diethylene triamine penta methyl phosphonic acid	-	-	0.6	-	-
Mg Sulfate	-	-	0.8	-	-
Photoactivated bleach	45	50	15	45	42
	ppm	ppm	ppm	ppm	ppm
Brightener 1	0.05	-	0.04	0.04	0.04
Brightener 2	0.1	0.3	0.05	0.13	0.13
Water and Minors			up to 100%		

Example 10

The following liquid detergent formulations, according to the present invention were prepared:

5

Example 11

5 Granular fabric cleaning compositions which provide "softening through the wash" capability were prepared in accord with the present invention :

	I	II
45AS	-	10.0
LAS	7.6	-
68AS	1.3	-
45E7	4.0	-
25E3	-	5.0
Coco-alkyl-dimethyl hydroxy-ethyl ammonium chloride	1.4	1.0
Citrate	5.0	3.0
Na-SKS-6	-	11.0
Zeolite A	15.0	15.0
MA/AA	4.0	4.0
DETPMP	0.4	0.4
PB1	15.0	-
Percarbonate	-	15.0
TAED	5.0	5.0
Smectite clay	10.0	10.0
HMWPEO	-	0.1
Mycodextranase	0.001	0.001
Protease	0.02	0.01
Lipase	0.02	0.01
Amylase	0.03	0.005
Cellulase	0.001	-
Silicate	3.0	5.0
Carbonate	10.0	10.0
Granular suds suppressor	1.0	4.0
CMC	0.2	0.1
Water/minors	Up to 100%	

Example 12

The following rinse added fabric softener composition was prepared in accord with the present invention :

5

Softener active	20.0
Mycodextranase	0.001
Amylase	0.001
Cellulase	0.001
HCL	0.03
Antifoam agent	0.01
Blue dye	25ppm
CaCl ₂	0.20
Perfume	0.90
Water / minors	Up to 100%

Example 13

10 The following fabric softener composition was prepared in accord with the present invention :

	I	II	III
DEQA	2.6	19.0	-
SDASA	-	-	70.0
Stearic acid of IV=0	0.3	-	-
Neodol 45-13	-	-	13.0
Hydrochloride acid	0.02	0.02	-
Ethanol	-	-	1.0
PEG	-	0.6	-
Mycodextranase	0.1	0.1	0.05
Perfume	1.0	1.0	0.75
Digeranyl Succinate	-	-	0.38
Silicone antifoam	0.01	0.01	-
Electrolyte	-	600ppm	-
Dye	100ppm	50ppm	0.01
Water and minors	100%	100%	100%

Example 14

Syndet bar fabric cleaning compositions were prepared in accord with the present invention :

5

	I	II	III	IV
C26 AS	20.00	20.00	20.00	20.00
CFAA	5.0	5.0	5.0	5.0
LAS (C11-13)	10.0	10.0	10.0	10.0
Sodium carbonate	25.0	25.0	25.0	25.0
Sodium pyrophosphate	7.0	7.0	7.0	7.0
STPP	7.0	7.0	7.0	7.0
Zeolite A	5.0	5.0	5.0	5.0
CMC	0.2	0.2	0.2	0.2
Polyacrylate (MW 1400)	0.2	0.2	0.2	0.2
Coconut monethanolamide	5.0	5.0	5.0	5.0
Mycodextranase	0.001	0.001	0.001	0.001
Amylase	0.001	0.001	0.001	0.001
Protease	0.03	-	0.05	0.005
Brightener, perfume	0.2	0.2	0.2	0.2
CaSO ₄	1.0	1.0	1.0	1.0
MgSO ₄	1.0	1.0	1.0	1.0
Water	4.0	4.0	4.0	4.0

Filler* : balance to 100%

*Can be selected from convenient materials such as CaCO₃, talc, clay (Kaolinite, Smectite), silicates, and the like.

Example 15

The following compact high density (0.96Kg/l) dishwashing detergent compositions I to VI were prepared in
5 accord with the present invention:

	I	II	III	IV	V	VI
STPP	-	-	49.0	38.0	-	-
Citrate	33.0	17.5	-	-	54.0	25.4
Carbonate	-	17.5	-	20.0	14.0	25.4
Silicate	33.0	14.8	20.4	14.8	14.8	-
Metasilicate	-	2.5	2.5	-	-	-
PB1	1.9	9.7	7.8	14.3	7.8	-
PB4	8.6	-	-	-	-	-
Percarbonate	-	-	-	-	-	6.7
Nonionic	1.5	2.0	1.5	1.5	1.5	2.6
TAED	4.8	2.4	2.4	-	2.4	4.0
HEDP	0.8	1.0	0.5	-	-	-
DETPMP	0.6	0.6	-	-	-	-
PAAC	-	-	-	0.2	-	-
BzP	-	-	-	4.4	-	-
Paraffin	0.5	0.5	0.5	0.5	0.5	0.2
Mycodextranase	0.01	0.05	0.01	0.05	0.01	0.05
Protease	0.075	0.05	0.10	0.10	0.08	0.01
Lipase	-	0.001	-	0.005	-	-
Amylase	0.01	0.005	0.015	0.015	0.01	0.0025
BTA	0.3	0.3	0.3	0.3	0.3	-
Bismuth Nitrate	-	0.3	-	-	-	-
PA30	4.0	-	-	-	-	-
Terpolymer	-	-	-	4.0	-	-
480N	-	6.0	2.8	-	-	-
Sulfate	7.1	20.8	8.4	-	0.5	1.0
pH (1% solution)	10.8	11.0	10.9	10.8	10.9	9.6

Example 16

The following granular dishwashing detergent compositions examples I to IV of bulk density 1.02Kg/L were
5 prepared in accord with the present invention :

	I	II	III	IV	V	VI
STPP	30.0	30.0	30.0	27.9	34.5	26.7
Carbonate	30.5	30.5	30.5	23.0	30.5	2.80
Silicate	7.4	7.4	7.4	12.0	8.0	20.3
PB1	4.4	4.4	4.4	-	4.4	-
NaDCC	-	-	-	2.0	-	1.5
Nonionic	0.75	0.75	0.75	1.9	1.2	0.5
TAED	1.0	1.0	-	-	1.0	-
PAAc	-	-	0.004	-	-	-
BzP	-	1.4	-	-	-	-
Paraffin	0.25	0.25	0.25	-	-	-
Mycodextranase	0.01	0.05	0.01	0.05	0.01	0.05
Protease	0.05	0.05	0.05	-	0.1	-
Lipase	0.005	-	0.001	-	-	-
Amylase	0.003	0.001	0.01	0.02	0.01	0.015
BTA	0.15	-	0.15	-	-	-
Sulfate	23.9	23.9	23.9	31.4	17.4	-
pH (1% solution)	10.8	10.8	10.8	10.7	10.7	12.3

Example 17

The following detergent composition tablets of 25g weight were prepared in accord with the present invention by 5 compression of a granular dishwashing detergent composition at a pressure of 13KN/cm² using a standard 12 head rotary press:

	I	II	III
STPP	-	48.8	47.5
Citrate	26.4	-	-
Carbonate	-	5.0	-
Silicate	26.4	14.8	25.0
Mycodextranase	0.01	0.05	0.01
Protease	0.03	0.075	0.01
Lipase	0.005	-	-
Amylase	0.01	0.005	0.001
PB1	1.6	7.8	-
PB4	6.9	-	11.4
Nonionic	1.2	2.0	1.1
TAED	4.3	2.4	0.8
HEDP	0.7	-	-
DETPMP	0.65	-	-
Paraffin	0.4	0.5	-
BTA	0.2	0.3	-
PA30	3.2	-	-
Sulfate	25.0	14.7	3.2
pH (1% solution)	10.6	10.6	11.0

Example 18

The following liquid dishwashing detergent compositions were prepared in accord with the present invention I to II, of density 1.40Kg/L :

	I	II
STPP	33.3	20.0
Carbonate	2.7	2.0
Silicate	-	4.4
NaDCC	1.1	1.15
Nonionic	2.5	1.0
Paraffin	2.2	-
Mycodextranase	0.01	0.01
Protease	0.03	0.02
Amylase	0.005	0.0025
480N	0.50	4.00
KOH	-	6.00
Sulfate	1.6	-
pH (1% solution)	9.1	10.0

Example 19

The following liquid hard surface cleaning compositions were prepared in accord with the present invention :

	I	II	III	IV	V	VI
Mycodextranase	0.001	0.005	0.001	0.005	0.001	0.005
Amylase	0.01	0.002	0.005	0.02	0.001	0.005
Protease	0.05	0.01	0.02	0.03	0.005	0.005
EDTA*	-	-	2.90	2.90	-	-
Citrate	-	-	-	-	2.90	2.90
LAS	1.95	-	1.95	-	1.95	-
C12 AS	-	2.20	-	2.20	-	2.20
NaC12(ethoxy)	-	2.20	-	2.20	-	2.20
**sulfate	-	-	-	-	-	-
C12 Dimethylamine	-	0.50	-	0.50	-	0.50
oxide	-	-	-	-	-	-
SCS	1.30	-	1.30	-	1.30	-
Hexyl Carbitol**	6.30	6.30	6.30	6.30	6.30	6.30
Water				Balance to 100%		

*Na4 ethylenediamine diacetic acid

15 **Diethylene glycol monohexyl ether

***All formulas adjusted to pH 7

Example 20

The following spray composition for cleaning of hard surfaces and removing household mildew was prepared in
5 accord with the present invention :

Mycodextranase	0.01
Amylase	0.01
Protease	0.01
Sodium octyl sulfate	2.00
Sodium dodecyl sulfate	4.00
Sodium hydroxide	0.80
Silicate (Na)	0.04
Perfume	0.35
Water/minors	up to 100%

Example 21

A two-layer effervescent denture cleansing tablet was prepared in accord with the present invention :

5

Acidic Layer

Mycodextranase	0.1
Protease	0.1
Tartaric acid	24.0
Sodium carbonate	4.0
Sulphamic acid	10.0
PEG 20,000	4.0
Sodium bicarbonate	24.5
Potassium persulfate	15.0
Sodium acid pyrophosphate	7.0
Pyrogenic silica	2.0
Tetracetylethylene diamine	7.0
Ricin-oleylsulfosuccinate	0.5
Flavor	1.0

Alkaline layer

PB1	32.0
Bicarbonate	19.0
EDTA	3.0
STPP	12.0
PEG 20,000	2.0
Potassium persulfate	26.0
Sodium carbonate	2.0
Pyrogenic silica	2.0
Dye/flavor	2.0

Example 22

Dentifrice compositions were prepared in accord with the present invention :

5

	I	II	III	IV
Sorbitol (70% aqueous solution)	35.000	35.000	35.000	35.000
PEG-6	1.000	1.000	1.000	1.000
Silica dental abrasive	20.000	20.000	20.000	20.000
Sodium fluoride	0.243	0.243	0.243	0.243
Titanium dioxide	0.500	0.500	0.500	0.500
Sodium saccharin	0.286	0.286	0.286	0.286
Mycodextranase	0.5	0.5	0.3	0.3
Protease	2.000	3.500	1.500	2.000
Sodium alkyl sulfate (27.9% aqueous solution)	4.000	4.000	4.000	4.000
Flavor	1.040	1.040	1.040	1.040
Carboxyvinyl polymer	0.300	0.300	0.300	0.300
Carrageenan	0.800	0.800	0.800	0.800
Water	Balance to 100%			

Example 23

10 Mouthwash compositions were prepared in accord with the present invention :

	I	II	III	IV
SDA 40 Alcohol	8.00	8.00	8.00	8.00
Flavor	0.08	0.08	0.08	0.08
Emulsifier	0.08	0.08	0.08	0.08
Sodium fluoride	0.05	0.05	0.05	0.05
Glycerin	10.00	10.00	10.00	10.00
Swe. etener	0.02	0.02	0.02	0.02
Mycodextranase	0.5	0.3	0.5	0.3
Protease	3.00	7.50	1.00	5.00
Benzoic acid	0.05	0.05	0.05	0.05
Sodium hydroxide	0.20	0.20	0.20	0.20
Dye	0.04	0.04	0.04	0.04
Water	Balance to 100%			

Example 24

A liquid personal cleansing composition containing soap was prepared in accord with the present invention :

5

	I	II
Mycodextranase	0.1	0.1
Protease	0.10	-
Soap (K or Na)	15.00	-
30% Laurate	-	-
30% Myristate	-	-
25% Palmitate	-	-
15% Stearate	-	-
Fatty acids (above ratios)	4.50	-
Na Lauryl Sarcosinate	6.00	-
Sodium Laureth Sulfate	0.66	12.0
Cocamidopropylbetaine	1.33	3.0
Glycerine	15.00	-
Propylene Glycol	9.00	-
Ethylene glycol distearate (EDTA)	1.50	0.38
Cocoamide MEA	-	0.2
Perfume	-	0.6
*Polyquaterium-7	-	0.08
DMDM hydantoin	-	0.14
Sodium benzoate	-	0.25
Tetrasodium EDTA dihydrate	-	0.11
Citric	-	0.09
Propylparaben	0.10	-
Methylparaben	0.20	-
Calcium sulfate	3	-
Acetic acid	3	-
Water and minors		Up to 100%
KOH/NaOH (pH adjustment)		

* Copolymer of dimethyl dialkyl ammonium chloride and acrylamide

Example 25

A personal cleansing bar composition was prepared in accord with the present invention :

5

Sodium Cocoyl Isethionate	47.20
Sodium Cetearyl sulfate	9.14
Paraffin	9.05
Sodium Soap (in situ)	3.67
Sodium Isethionate	5.51
Sodium Chloride	0.45
Titanium Dioxide	0.4
Trisodium EDTA	0.1
Trisodium Etidronate	0.1
Perfume	1.20
Na ₂ SO ₄	0.87
Mycodextranase	0.5
Protease	0.10
Water	Balance to 100

Example 26

A shampoo composition was prepared in accord with the present invention :

5

	I	II	III	IV	V	VI
NH4 laureth-3 sulfate	16.0	18.0	10.0	16.0	14.0	18.0
NH4 lauryl sulfate	5.0	6.0	3.0	3.0	4.0	6.0
Na lauryl sarcosinate	-	-	2.0	-	-	-
Cocoamide MEA	1.0	-	-	1.0	0.6	-
Dimethicone 40/60	0.8	1.0	0.4	3.0	2.0	1.0
Polyquaternium-10	-	-	0.01	-	0.2	-
Cetyl alcohol	0.5	0.4	-	0.4	0.4	0.1
Stearyl alcohol	-	0.2	-	0.5	0.1	0.2
Panthenyl ethyl ether	0.2	-	-	0.2	0.2	0.2
Panthenol 10%	-	0.03	-	0.03	-	-
Tallow	-	-	-	-	-	0.5
Mineral oil	-	-	-	-	0.5	-
Tetrasodium EDTA	0.09	0.09	0.07	0.09	0.09	0.09
DMDM Hydantoin	0.14	0.14	0.14	0.12	0.14	0.14
Sodium benzoate	0.25	0.25	-	0.25	0.25	0.25
Citrate	1.0	-	-	1.0	1.0	-
Citric	0.1	-	0.3	0.1	-	-
Sodium hydroxide	-	-	0.3	-	-	-
Sodium phosphate	-	0.6	-	-	-	0.6
Disodium phosphate	-	0.2	-	-	-	0.2
Sodium chloride	1.5	1.5	3.0	1.5	2.0	1.5
PEG-12	-	-	0.15	-	-	0.4
NH4 xylene sulfonate	0.4	0.4	-	0.4	0.4	0.4
Glycol distearate	1.0	3.0	1.5	2.0	3.0	0.5
Zinc pyrithione	-	-	1.0	-	-	-
Mycodextranase	0.05	0.05	0.05	0.05	0.05	0.05
Perfume	0.2	0.6	0.6	0.2	0.4	0.6
Water and minors				Up to 100%		

What is claimed is:

1. A cleaning composition comprising a mycodextranase enzyme.
2. The cleaning composition according to Claim 1, wherein said mycodextranase enzyme is present at a level of from about 0.00001% to about 1% as a pure enzyme by weight of composition.
3. The cleaning composition according to Claim 1 further comprising one or more enzymes selected from the group consisting of protease, lipase, cellulase, amylase, and the like.
4. The cleaning composition according to Claim 1 further comprising one or more surfactants selected from the group consisting of nonionic, anionic, cationic, zwitterionic, amphoteric or mixtures thereof.
5. The cleaning composition according to Claim 1 further comprising one or more components selected from the group consisting of bleaching agents, suds suppressors, soil suspension and anti-redeposition agents, soil release polymer, smectite clays, builder components and the like.
6. The cleaning composition according to Claim 1 characterized in that said composition is in the liquid, paste, gel, bar, tablet, powder or granular form.
7. The cleaning composition according to Claim 1 characterized in that the composition further comprises no more than about 15% by weight of inorganic filler salt.

8. The cleaning composition according to Claim 1 characterized in that the composition is a heavy duty liquid detergent composition.

9. A detergent additive comprising a mycodextranase enzyme.

10. Use of a cleaning composition according to claims 1 to 5 for fabric cleaning and/or fabric stain removal and/or fabric whiteness maintenance and/or fabric softening and/or fabric color appearance and/or fabric dye transfer 5 inhibition.

11. Use of a cleaning composition according to claims 1 to 5 for cleaning hard surfaces such as floors, walls, bathroom tile and the like.

12. Use of a cleaning composition according to claims 1 to 5 for hand and machine dishwashing.

13. Use of a cleaning composition according to claims 1 to 5 for oral, dental, contact lenses and personal cleaning applications.

14. A detergent composition comprising:

(a) from about 0.1% to about 60% detergent surfactant selected from the group consisting of nonionic, anionic, cationic, zwitterionic, amphoteric surfactant, and mixtures 5 thereof, by weight of composition;

(b) from about 0.00001% to about 1% pure mycodextranase enzyme by weight of composition; and

(c) no more than about 15% by weight of inorganic filler salt.

10

15. The detergent composition according to Claim 14, comprising:

- (a) from about 1% to about 35% detergent surfactant selected from the group consisting of nonionic, anionic, 5 cationic, zwitterionic, amphoteric surfactant, and mixtures thereof, by weight of composition;
- (b) from about 0.0001% to about 0.5% pure mycodextranase enzyme by weight of composition; and
- (c) one or more components selected from the group 10 consisting of bleaching agents, suds suppressors, soil suspension and anti-redeposition agents, soil release polymer, smectite clays, builder components and the like.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 96/15572

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D3/386

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 425 017 A (THE PROCTER & GAMBLE CO. ; GENENCOR INTERNATIONAL INC.) 2 May 1991 see page 3, line 45 - line 50 see page 13, line 25 - line 45 see page 17, line 44 - page 18, line 27 ---	1,3-7, 10,11,13
A	US 4 710 313 A (MIYAJIMA NOBUYUKI ET AL.) 1 December 1987 see abstract ---	1,3,13
A	US 4 138 476 A (SIMONSON LLOYD G. ET AL.) 6 February 1979 see column 3, line 8 - line 34 see claims 1,4,11,15,20 ---	1,13

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/15572

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>CHEMICAL ABSTRACTS, vol. 76, no. 11, 13 March 1972 Columbus, Ohio, US; abstract no. 55830, TUNG, K. K. ET AL: "Enzymes that hydrolyze fungal cell wall polysaccharides. II. Purification and properties of mycodetranase, an endo-.alpha.-D-(1->4)glucanase from <i>Penicillium melinii</i>" XP002031712 cited in the application see abstract & J. BIOL. CHEM. (1971), 246(22), 6722-36 CODEN: JBCHA3, -----</p>	1

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Information on patent family members

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PCT/US 96/15572

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